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Rhodesite, a new mineral from the Bultfontein mine, Kimberley.

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[Taken as read 28 March 1957.]

Summary. A small specimen at first thought to be natrolite has proved to be a new mineral, for which the name rhodesite is proposed; it is fibrous, with α 1·502, β 1·506, γ 1·515, elongation γ, extinction straight, sp. gr. 2·36. The composition is near $4(Ca,Na_2,K_2)O \cdot 10SiO_2 \cdot 7H_2O$, and the water is all zeolitic.

A MINERAL specimen was sent to me in 1938 by Miss M. Wilman, then Director of the McGregor Museum, Kimberley. It weighed about 200 gm., appeared to be fairly uniform in character, and was reported as coming from the Bultfontein Mine. In reply to her, I reported that it had many properties close to those of natrolite, a common zeolite, but that it differed in some essential details and also in general appearance. I sent a sample to Dr. F. A. Bannister of the British Museum asking if he would examine it by X-rays, and retained the bulk of the specimen with the intention of making a careful chemical analysis if it could not be identified.

Dr. Bannister reported that the powder photograph was not very clear and that he was unable to identify the mineral. He promised to examine it more carefully when he had time, but this was never done owing to the war and Dr. Bannister's illness. Subsequently I learnt that the material sent to him had been mislaid.

I made a rough chemical analysis, which showed that the mineral was a hydrated silicate of lime and alkalis with a silica percentage about 62 and a little alumina. This was quite different from natrolite which has a silica percentage of 47 and an alumina percentage about 27. At the end of 1954 Dr. H. F. W. Taylor of Aberdeen University undertook to

examine the mineral by X-rays and subsequently arranged for a differential thermal analysis. He will publish his detailed results separately, but has meanwhile sent me a summary of his results and confirms that the mineral is an undescribed species.

The specimen is a mass of matted silky white fibres, with a suggestion of subradiating texture, in the form of rosettes up to 2 mm. in size. Under the microscope individual fibres are not more than 0·5 mm. in length and some of them are slightly platy suggesting a possible cleavage parallel to the length. The specimen is macroscopically fairly uniform and looks as though it consists almost entirely of one mineral with the exception of a few minor grey-green patches probably consisting of serpentine typical of the Kimberlite of the mine. There is, however, a suggestion on the freshest face of the specimen that one-half of the specimen is slightly more silky than the other and thus possibly less altered. It was this material that was consequently selected for more detailed examination and some 10 g. were picked out for chemical, optical, and other tests. These tests showed that the selected material was in fact homogeneous whereas the other half of the specimen proved subsequently to consist to a large extent of a very similar but optically distinct species.

The hardness could not be determined accurately owing to the fineness of the fibres and the tendency of the fibres to tear apart instead of being scratched. On massive material, however, it appears to be about 4. The specific gravity also presented a problem. By the suspension method a figure of 2·31 was obtained for the little rosettes, but the individual fibres showed variation in sinking. A small diffusion column prepared in a test-tube showed that in general the tiniest fibres sank first and the larger aggregates last. This suggested that the aggregates enclosed a certain amount of air. The first appreciable crop of fibres to sink proved to have a specific gravity of 2·36, while some of the larger aggregates corresponded to less than 2·30. Results obtained by pycnometer were very variable and were probably affected by absorption of water. When air was boiled off, the figures obtained were round about 2·38. The figure of 2·36, however, seems to be most acceptable.

On ignition, fibres are fusible to a clear glass of refractive index about 1·532. This material is mostly colourless but in places stained a pale brown as though iron is originally distributed irregularly through the mineral. Water heated with the mineral gives a strong alkaline reaction with an indicator and on heating with concentrated hydrochloric acid the mineral quickly decomposes leaving a silica gel.

Single fibres under the microscope have straight extinction always with length slow whereas much of the material in the other half of the specimen is elongated along the β vibration direction. In the latter case there appear roughly equal numbers of fibres under the microscope showing length fast and slow respectively, and individually they can be distinguished from the mineral being described by the fact that when fibres are rotated about their length they change sign of elongation. These fibres are in general shorter and less distinct. Dr. Taylor has done a considerable amount of work on this latter mineral and believes it also to be an undescribed species. In fact the specimen first examined by him consisted largely, if not entirely, of this second mineral.

The refractive indices determined by immersion were found to be α 1·502, β 1·506, γ 1·515, so that the mineral is presumably orthorhombic. The cleavage previously mentioned appears to be normal to the β-vibration, but although oriented sections were prepared no recognizable interference figure could be obtained in any orientation. The determination of β was not very accurate owing to the composite nature of the fibres, but at least it seems probable from the value of β obtained that the mineral is optically positive.

Chemical analyses made on the material used for the physical properties gave the following results. On crushing, the mineral cannot be sieved, but aggregates into small spherical masses like short-fibre asbestos.

	1.	2.	Average.	Molecular ratios.	
SiO_2	61·79	61·86	61·83	1030	
Al_2O_3	0·30	0·28	0·29	3	
FeO	0·25	0·25	0·25	3	
CaO	14·95	14·85	14·90	266	
MgO	0·09	0·07	0·08	2	407
Na_2O	5·04	4·82	4·93	80	
K_2O	5·40	5·16	5·28	56	
H_2O	12·45	12·55	12·50	694	
	100·27	99·84	100·06		

Analysis 1 was made by fusion methods before it was realized that the mineral could be decomposed with acid. Analysis 2 was made after decomposition with hot concentrated hydrochloric acid. Chemical tests on other samples suggest that the lime can be as high as 18 % and the alkalis correspondingly low. The analyses were made on air-dried material so that the water represents total water. It is impossible to give a simple figure for hygroscopic water as the amount driven off at 110° C. varies so much with time.

Mr. J. B. Hawthorne of Rhodes University carried out some preliminary dehydration experiments on the mineral. After prolonged heating at 110° C. the loss of water was determined as 4·14 %, and on subsequent cooling all the water was recovered under room conditions in about 12 hours. On heating at 275° C. practically all the water was driven off within 20 minutes and after cooling most of the water was recovered after 8 hours, but about 1 % of the water remained unrecovered. As stated previously, on ignition the mineral melts and then no water is recovered on cooling. The dehydration curve for different temperatures is almost a uniform curve and there is no well-defined change of slope.

The composition corresponds roughly to $4(Ca,Na_2,K_2)O.10SiO_2.7H_2O$ with a molecular ratio CaO:alkalis about 2:1.

All these properties are similar to those of certain zeolites, especially the natrolite-thomsonite group, but the mineral differs chemically from the zeolites in containing virtually no alumina and in having a low oxygen/silicon ratio of 2·4. Pure natrolite, for example, contains 27 % alumina and has an oxygen/silicon ratio of 3·3. Amongst the allied minerals, however, the nearest approach seems to be okenite which contains no alumina and has an oxygen/silicon value of 2·5. Its composition is given as $H_2CaSi_2O_6.H_2O$. Its physical properties are rather similar, but its refractive indices are given as 1·530–1·541 which is well outside the range of the present mineral, while the virtual absence of alkalis in okenite also shows that it is quite distinct.

For this new mineral I suggest the name *Rhodesite* (pronounced rōdzite). It would seem to be suitable in view of the close connexion between C. J. Rhodes and Kimberley and also after Rhodes University where the mineral has been examined.

Finally it may be of interest to note that Bultfontein, one of the Kimberley diamond mines, is already the source of another new mineral bultfonteinite $2Ca(OH,F)_2.SiO_2$ described by Parry, Williams, and Wright in 1932. It had previously been referred to as dutoitspanite by Williams in his book 'The Genesis of the Diamond', but this earlier name was apparently discarded. Bultfonteinite was accompanied by another new but undescribed mineral, a hydrous calcium sulphate.

An investigation of two new minerals: rhodesite and mountainite.

By J. A. Gard, B.Sc., Ph.D., and H. F. W. Taylor, D.Sc., Ph.D., with chemical analyses by R. A. Chalmers, B.Sc., Ph.D.

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[Read 1 November 1956.]

Summary. Rhodesite, from Kimberley, S. Africa, has been examined by electron-microscope, X-ray, and other methods. The acicular crystals are orthorhombic, with a 23·8, b 6·54, c 7·05 Å.; elongation c, cleavage (100); unit-cell contents approximately $(Ca,Na_2,K_2)_8Si_{16}O_{40}.11H_2O$; optical properties α 1·502, β 1·505, γ 1·515; $\alpha = b$, $\beta = a$, $\gamma = c$. With it occurs a similar but distinct fibrous mineral, which appears to be a new species for which the name *mountainite* is proposed; it is monoclinic, with a 13·51, b 13·10, c 13·51 Å., β 104°; elongation b, cleavage (001); unit-cell contents approximately $(Ca,Na_2,K_2)_{16}Si_{32}O_{80}.24H_2O$; optical properties α 1·504, β 1·510, γ 1·519; $\beta = b$ (elongation). Both rhodesite and mountainite show close similarities to the fibrous zeolites, mountainite in particular resembling thomsonite. The possible structural basis of these similarities is discussed.

E. D. MOUNTAIN (1957) has recently described the new mineral rhodesite, including details of its occurrence, chemical composition (approximately $4(Ca,Na_2,K_2)O.10SiO_2.7H_2O$), optical properties, and behaviour on dehydration and rehydration. Prof. Mountain very kindly provided several portions of his specimen for crystallographic investigations, and the results of these form the subject of the present paper.

Several pieces of material were examined, weighing in all a few grams. All consisted of matted white fibres. To test whether the material was homogeneous, powder specimens and also several tens of individual fibres were taken from different parts of the specimen, and were examined using optical, X-ray powder and single-crystal, and electron-microscope methods. The results showed that two species were present, similar in appearance and optical properties. One was subsequently identified with rhodesite from its chemical analysis and sign of elongation. The other appears to be a further new species, for which the name *mountainite* is proposed (pronounced with the *ou* as in *house*). Some of the pieces examined consisted almost wholly of one or the other mineral; in others, both were present.[1]

[1] The original portion sent by Prof. Mountain happened to consist almost wholly of mountainite. This was wrongly assumed to be rhodesite and described as such at the November 1956 meeting of the Mineralogical Society (Notice of Meeting, No. 95).

Optical data found for the two species in the present investigation are given in table I. The data for rhodesite agree closely with those reported by Mountain.

TABLE I. Optical and unit-cell data for rhodesite and mountainite.

	Rhodesite.	Mountainite.
Optical properties:		
Appearance:	White fibres (length c). Larger and better crystallized than those of mountainite. Laths $500 \times 100 \times 50$ μ appeared to be single crystals though subsequent X-ray examination showed considerable angular spread of all reflections	White fibres (length b). Even the smallest visible were polycrystalline, though ones of $400 \times 20 \times 10$ μ approximated to single crystals
Cleavage:	One good cleavage (100) in the prism zone	One doubtful cleavage in the prism zone
Extinction:	Parallel: + elongation (γ)	Parallel: $\pm$ elongation (β)
Indices (Na):	α 1·502	α 1·504*
	β 1·505	β 1·510
	γ 1·515	γ 1.519*
Orientation:	$b = \alpha$	
	$c = \gamma$ (elongation)	$b = \beta$ (elongation)
	$a = \beta$ (normal to cleavage)	
Optic sign and 2V:	Probably + with low 2V	Probably + with moderate or high 2V
Unit-cell data:†		
Crystal system:	Orthorhombic.	Monoclinic.
a	23·8 Å.	13·51 Å.
b	6·54 Å.	13·10 Å.
c	7·05 Å.	13·51 Å.
β	90°	104°
Cell contents:	$(Ca,Na_2,K_2)_8Si_{16}O_{40}.11H_2O$	$(Ca,Na_2,K_2)_{16}Si_{32}O_{80}.24H_2O$

* True single crystals of mountainite might be expected to have α lower and γ higher than these values.

† The parameters given are considered the most probable ones, but for mountainite the true value of b may be 6·55 Å. and for rhodesite the cell given may be a pseudo-cell; see Discussion.

Electron-microscope investigation. Fibres of each species were identified from X-ray oscillation photographs and then crushed lightly in water. Drops of the resulting suspensions were allowed to dry on specimen grids coated with formvar films, and examined using a Metropolitan-Vickers EM-3 electron microscope. Some specimens were shadow-cast with gold-palladium alloy.

A typical electron micrograph of *rhodesite* is shown in fig. 1. The

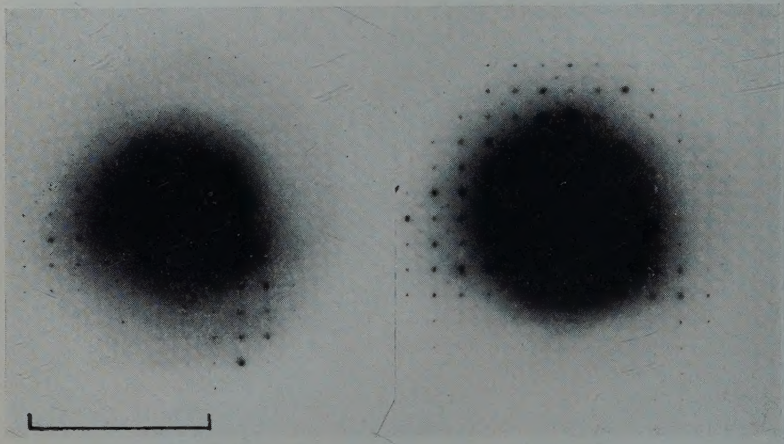
particles were elongated laths, which in many cases had one end pointed. The electron-diffraction patterns (fig. 2) faded quickly in the electron beam, but examination was made possible by use of the specimen screening aperture described by Page and Agar (1954). If the fibre axis is called

FIG. 1. Electron micrograph of rhodesite, showing laths with elongation *c* and principal cleavage (100). Some crystals have one end pointed. × 4 000.

c, and the principal cleavage (100), the electron-diffraction data give the mean values *b* 6·57, *c* 7·00 Å., α 90°. Most patterns were intersected by Laue zones if the crystals were tilted. The relative positions of the reflections in adjacent zones indicated a primitive lattice, and application of a procedure described elsewhere (Gard, 1956) gave a mean value of 25 Å. for *a*. The zero-order Laue zone was usually nearly central when the specimen grid was normal to the electron beam, as shown in fig. 2*a*, indicating that the *a*-axis is probably normal to (100), and the unit cell

is orthorhombic. Some of the patterns, one of which is shown in fig. 2*b*, had weak reflections at the face-centres of the typical spot pattern, which suggests that the true unit cell may be A-centred with doubled values for *b* and *c*. The intensity of this pattern of weak reflections varied from one crystal to another.

The electron-diffraction results, therefore, give the following provi-



(*a*) (*b*)

FIG. 2. Electron-diffraction patterns from single crystals of rhodesite with (100) approximately normal to the beam. Zero- and first-order Laue zones are present in each case. (*a*) Typical pattern with no superlattice reflections. The lattice is primitive. (*b*) Pattern with weak superlattice reflections giving doubled values of *b* and *c*. The scale represents 1 Å.$^{-1}$.

sional unit-cell data for rhodesite: orthorhombic; *a* 25, *b* 6·57, *c* 7·00 Å.; elongation *c*, principal cleavage (100); some indication of a superlattice with doubled values of *b* and *c*.

A typical electron micrograph of *mountainite* is shown in fig. 3. The specimen consisted of laths of rectangular outline, with their principal cleavage faces lying on the supporting film. The laths were less elongated than with rhodesite. Similar electron-diffraction patterns, of which fig. 4 is typical, were given by most of the crystals. The patterns did not fade quickly, and the mineral therefore appears to be stable in the electron beam. If the cleavage is called (001) and the prism axis *b*, the patterns give mean values of *a* 13·7, *b* 13·1 Å., γ 90°. These patterns appeared to be divided into Laue zones parallel to the *b*-axis. The centres of the zones were too far from the direct electron-beam spot to be located,

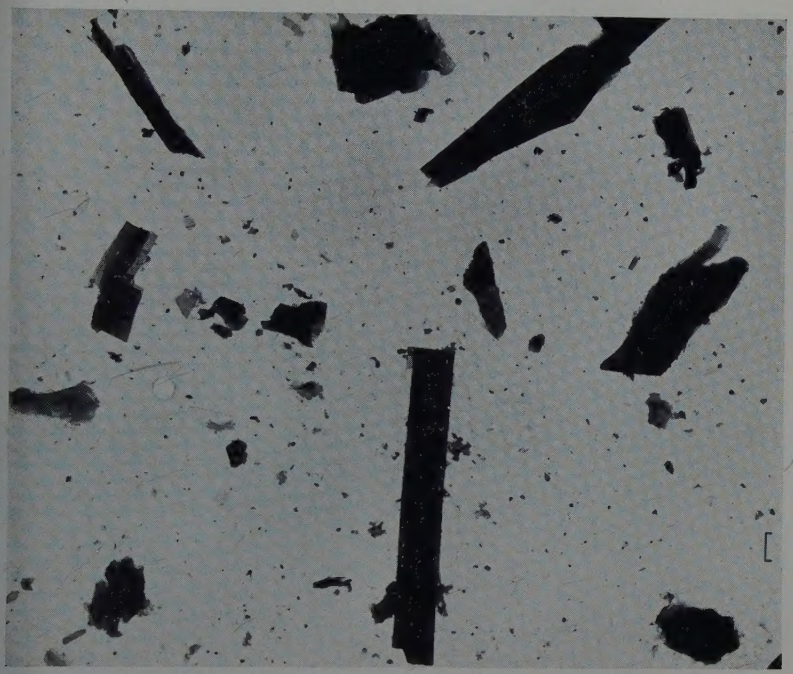


FIG. 3. Electron micrograph of mountainite showing rectangular laths with elongation b and principal cleavage (001). × 4 000.

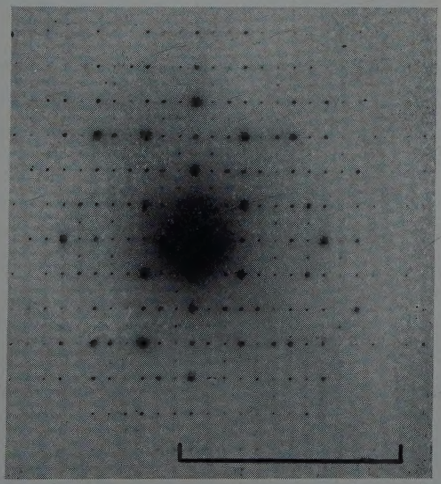
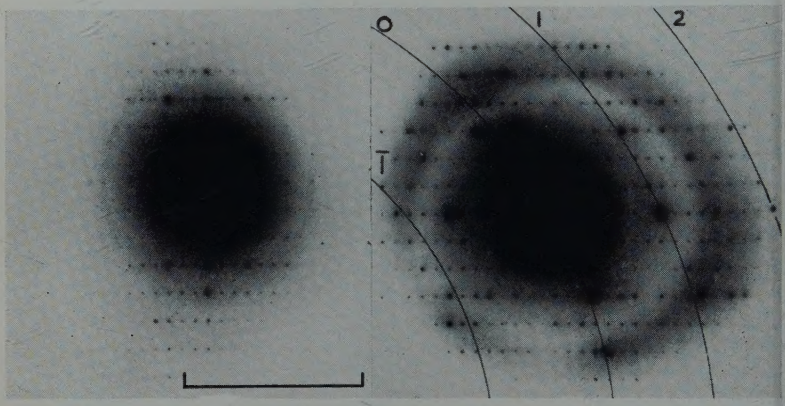


FIG. 4. A typical electron-diffraction pattern from a single crystal of mountainite, with (001) normal to the electron beam. Alternate strong and weak layer-lines are visible for even and odd values of k. The scale represents 1 Å.$^{-1}$.

even when the crystals were tilted through the maximum angle (*c.* 7°) possible in the tilt block of the specimen stage. This indicated that *b* coincides with *b**, but that the angle between *a* and *a** is much greater than 7°. The unit cell is thus monoclinic, and β exceeds 97°. Two fibrous crystals were lying with sufficient tilt about the fibre axis to give distinct Laue zones, as shown in fig. 5 *a* and *b*, and the relative positions of spots in adjacent zones indicated a primitive lattice. The procedure



(*a*) (*b*)

FIG. 5. Electron-diffraction patterns from the same crystal of mountainite: (*a*) with the *c*-axis nearly parallel to the electron beam; the *hk*0 Laue zone is almost central; (*b*) with the *c*-axis inclined at a few degrees to the beam; zero-, first-, and second-order Laue zones are visible and values of *l* are marked. The scale represents 1 Å.$^{-1}$.

described by Gard (1956) for the estimation of the third-row lattice spacing gave values of 12·8 and 10·9 Å. for *c*. All reflections with *k* odd were weak, and 0*k*0 reflections with *k* odd were absent. No other systematic absences were observed. 040, 080, 320, and 360 reflections appeared to be stronger than the others. These reflections fall on a face-centred sub-lattice with *a* 4·6, *b* 6·55 Å., and may be related to the positions of the heaviest, i.e. the calcium and potassium atoms, projected on the (001) plane.

The electron-diffraction results thus give the following provisional unit-cell data for mountainite: monoclinic, *a* 13·7, *b* 13·1, *c* 12$\pm$1 Å., $\beta > 97°$; elongation *b*, principal cleavage (001); strong pseudo-halving of *b*.

X-ray investigation. Rotation, oscillation, and equatorial Weissenberg photographs about the prism axis were obtained for both species.

In both cases, even though small crystals ($200 \times 20 \times 10\,\mu$) were used, reflections showed considerable angular spread, especially in the sense of rotation around the prism axis. Because of this, Weissenberg photographs were rather indefinite, as were any photographs taken with the crystals mounted about other axes. It was nevertheless found possible to determine the unit cells (or possibly pseudo-cells) from the oscillation and rotation photographs about the prism axes. The following results were obtained:

Rhodesite: orthorhombic; a 23·8, b 6·54, c 7·05 Å.; elongation c, principal cleavage (100).

TABLE II. X-ray powder data for rhodesite and mountainite, and for mountainite after heating at 275° C.

Rhodesite. Observed.		Calc.		Mountainite. Observed.		Calc.		Mountainite (heated). Observed.	
d (Å.)	I.	hkl.	d (Å.)	d (Å.)	I.	hkl.	d (Å.)	d (Å.)	I.
11·8	s	200	11·9	13·1	s	001	13·11	11·3	m
7·1	vw/d	001	7·05			$20\bar{1}$	6·59		
6·7		101	6·76	6·6	vs	200	6·55	6·4	vw
						020	6·55		
6·56	s	010	6·54			002	6·55		
6·28	w	110	6·32	5·9	vw	021	5·87	5·73	m
5·95	m	400	5·95			120	5·87		
5·25	vw	301	5·27	5·4	vw	201	5·40		
5·04	w	310	5·04			$20\bar{2}$	5·38		
4·80	w	011	4·79	4·67	s	022	4·65	4·34	vw
4·42	m	410	4·42			$22\bar{1}$	4·65		
4·11	vw	311	4·11	4·18	m	221	4·17	4·06	vw
3·99	vw	600	3·97			$22\bar{2}$	4·15		
		501	3·95	3·74	w	$32\bar{1}$	3·72		
3·87	vvw	510	3·85	3·66	w	023	3·66	3·9	vw/d
3·76	vvw	411	3·73			320	3·66		
3·51	vvw	002	3·53	3·36	mw	123	3·35		
3·39	w	610	3·39			203	3·31		
3·27	vw	020	3·27	3·30	w	$20\bar{4}$	3·29		
3·07	vs	112	3·08			$40\bar{2}$	3·29		
3·02	s	320	3·02			400	3·28		
		710	3·02	3·28	mw	040	3·28		
						004	3·28		
2·98	m	800	2·98	3·18	vw	$32\bar{3}$	3·16		
		021	2·97	3·04	vw	$12\bar{4}$	3·02	3·04	w
2·89	s	420	2·87			420	2·95		
		312	2·89			024	2·95		
2·78	s	321	2·78	2·94	vvs	$42\bar{2}$	2·95	2·86	w
		711	2·77			$22\bar{4}$	2·95		
2·75	ms	801	2·74			223	2·95		
		412	2·75			240	2·94		
				2·80	ms			2·76	w

TABLE II (*cont.*).

Rhodesite.		Mountainite.		Mountainite (heated).		Rhodesite.		Mountainite.	
d (Å.)	*I.*	*d* (Å.)	*I.*	*d* (Å.)	*I.*	*d* (Å.)	*I.*	*d* (Å.)	*I.*
2·72	vvw					1·488	vw	1·495	vvw
2·67	vvw					1·453	vw/b	1·463	mw
2·63	vvw	2·65	w			1·415	w	1·436	vw
2·53	w	2·54	w			1·373	vvw/d	1·391	vw
2·49	vvw					1·368	mw	1·363	vvw
2·44	vw	2·42	vw			1·343	vw	1·342	vvw
2·25	vvw	2·32	mw			1·320	vw	1·323	w
2·20	vvw	2·23	vw			1·300	vw/d		
2·15	w					1·291			
2·10	vvw	2·11	mw/d			1·275	w		
2·05	w					1·266	vvw	1·261	w
1·967	vw	1·967	ms			1·246	vw		
1·924	vw					1·231	vw		
1·890	vw	1·882	vw			1·222	vvw	1·226	vw
1·861	ms			1·86	vvw	1·206	vw		
1·840	vw					1·193	vvw		
1·815	vw	1·820	w			1·181	vvw	1·187	vw
1·771	vw/d			1·76	vvw	1·162	mw/b	1·162	vvw
1·756	ms					1·154	vvw	1·151	w
1·724	vvw	1·719	m			1·133	vvw	1·130	vvw
1·697	m					1·119	vvw	1·112	vw
1·695	m					1·108	vvw		
1·675	vw	1·678	vw			1·086	vvw	1·091	vw
1·650	vvw					1·067	vvw	1·074	vw
1·640	vvw	1·639	w			1·054	vvw	1·038	vvw
1·603	w					1·034	vvw	1·018	vvw
1·542	mw	1·578	vw			1·021	vw	1·011	vvw
1·522	vw							0·974	vw
1·501	vw							0·956	vvw

Mountainite: monoclinic; *a* 13·51, *b* 6·55, *c* 13·51 Å.; β 104°; elongation *b*. No low-order *h*0*l* reflections were detected.

X-ray powder data (table II) were obtained for each mineral using Cu-$K\alpha$ radiation with cameras of 6 cm. and 11·46 cm. diameter. In each case the low-angle reflections were indexed from direct superposition of powder and single-crystal photographs. Indices and calculated spacings given in table II relate to the unit cells given above, except that for mountainite a doubled value of *b* (13·10 Å.) was assumed on the basis of the electron-diffraction result. No powder lines were observed with either mineral that could not be accounted for on the single-crystal photographs; the powder data in each case, therefore, relate to substantially pure material.

Chemical analyses and unit-cell contents. Chemical analyses were kindly

made by Dr. R. A. Chalmers of specimens of each mineral, whose purity had been checked optically and by X-ray powder photographs. Table III gives the results for rhodesite (col. 2) and for mountainite (col. 3). The mean of Mountain's two analyses of rhodesite is also included (col. 1).

Specific gravities of the two specimens analysed in this investigation were determined by suspension in bromoform-benzene mixtures, care

TABLE III. Chemical analyses and unit-cell contents for rhodesite and mountainite.

	1.	2.	3.		4.	5.
SiO_2	61·83	61·6	58·5	Si	16·3	32·2
Al_2O_3	0·29	nil	nil	Al	—	—
FeO	0·25	nil	n.d.	Fe	—	n.d.
CaO	14·90	15·1	13·4	Ca	4·3	7·9
MgO	0·08	nil	0·2	Mg	—	0·2
Na_2O	4·93	5·2	7·9	Na	2·7	8·4
K_2O	5·28	6·0	6·0	K	2·0	4·3
H_2O	12·50	12·3*	13·4	H_2O	10·9	24·7
	100·06	100·2	99·4	O (not as H_2O)	39·2	79·8
Sp. Gr.	2·36	2·36	2·36	—	—	—

* Total loss on ignition; may include a little CO_2.

1. Rhodesite. E. D. Mountain (1957). Mean of two analyses.
2 and 3. Rhodesite and Mountainite. Analyses of present specimens by Dr. R. A. Chalmers.
4. Atomic cell-contents calculated from analysis 2.
5. Atomic cell-contents calculated from analysis 3.

being taken to remove air by preliminary evacuation. From the unit-cell, analytical, and specific gravity data, atomic cell-contents were calculated for rhodesite (col. 4) and mountainite (col. 5). For this purpose the unit-cell dimensions found using X-rays were used, except that for mountainite a doubled value of b (13·10 Å.) was assumed in view of the electron-diffraction evidence.

For rhodesite the unit-cell contents approximate to 16 Si, 8 ($Ca+Na_2+K_2$), 11 H_2O, and 40 O (not as H_2O). For mountainite they approximate to 32 Si, 16 ($Ca+Na_2+K_2$), 24 H_2O, and 80 O (not as H_2O).

Dehydration. Some preliminary crystallographic observations have been made on crystals of each mineral after heating at various temperatures. With rhodesite no change was detected in crystals heated at 500° C. On ignition the crystals melted to a glass which gave a weak X-ray powder pattern of pseudo-wollastonite (α-$CaSiO_3$). With moun-

tainite no change was detected in a crystal heated at 160° C. Crystals heated at 275° C. gave a weak pattern showing only slight preferred orientation. X-ray powder data for material so heated are given in table II. A crystal heated at 400° C. gave a weak and diffuse pattern

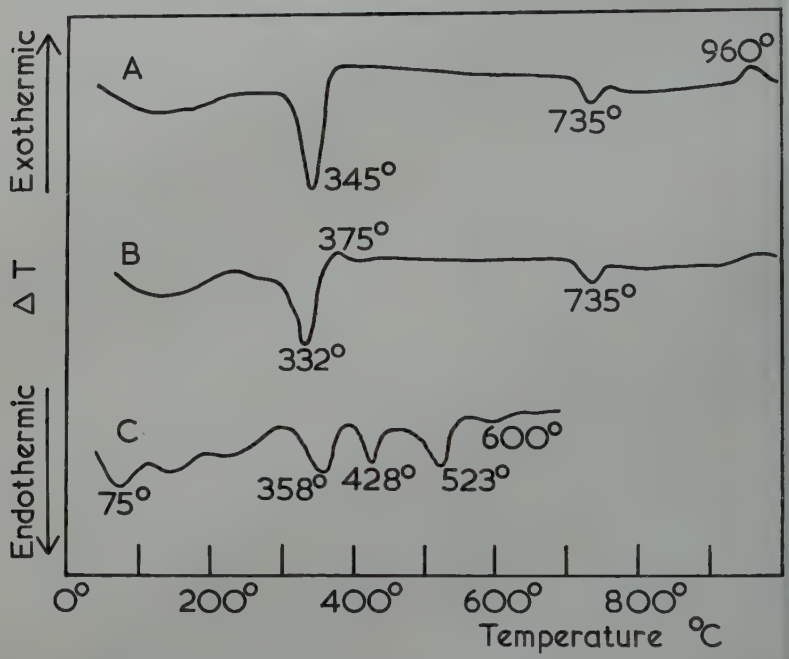


Fig. 6. Differential thermal analysis curves for A, rhodesite; B, mountainite; C, thomsonite. Curves A and B determined by Dr. R. C. Mackenzie (Macaulay Institute for Soil Research, Aberdeen); heating rate 10 deg./min. Curve C from M. Koizumi (1953); heating rate 2–3 deg./min.

similar to that obtained at 275° C.; one heated at 1000° C. melted to a glass that gave a weak pattern of β-$CaSiO_3$ with indications of much amorphous material.

D.T.A. curves for both minerals (fig. 6) were kindly determined by Dr. R. C. Mackenzie (Macaulay Institute for Soil Research, Aberdeen). One for thomsonite is included for comparison.

Discussion

The status of rhodesite and mountainite as mineral species. The present results show that rhodesite and mountainite are species distinct from each other. Although similar in composition and in optical properties,

there are significant differences in the latter, especially in the signs of elongation and in the indices for light vibrating parallel to the elongation. It is uncertain whether the differences between the chemical analyses are diagnostic because of the possibilities of variable composition in both cases. The two minerals are quite distinct crystallographically, and can readily be distinguished by X-ray powder photographs, or by single-crystal X-ray or electron-diffraction patterns.

Neither mineral could be correlated with any previously known species, excepting of course that described by Mountain. Rhodesite is therefore confirmed as a new species, and mountainite is shown to be an additional one.

Unit-cell data. For rhodesite, the electron-diffraction and X-ray results are in substantial agreement, and the X-ray values can be accepted as the more accurate. Electron diffraction gives indication of a superlattice for some crystals. The variable intensity of the superlattice pattern suggests that the degree of order may vary from crystal to crystal, or that it may be affected by exposure to the electron beam.

For mountainite, the X-ray results establish a pseudo-cell (a 13·51, b 6·55, c 13·51 Å., β 104°) with certainty, but there is some doubt as to the true cell and space-group because of three discrepancies between X-ray and electron-diffraction results, viz.: the electron-diffraction data show intermediate weak layer-lines corresponding to a doubled value (13·10 Å.) for b; the X-ray data give a precise value for c, but electron-diffraction suggests an indefinite and lower value; and low-angle $h0l$ reflections cannot be detected using X-rays but are not particularly weak on the electron-diffraction patterns.

These differences could be explained in either of two ways. It could be assumed that the crystals are unaltered in the electron microscope, except possibly for lattice shrinkage in the c-direction, and the discrepancies attributed to the fact that the electron-diffraction method is the more sensitive for detection of weak reflections, but less accurate than X-ray diffraction for determination of lattice parameters. In this case the true unit cell is monoclinic with a 13·51, b 13·10, c 13·51 Å., β 104°, and the true space-group $P2_1$ or $P2_1/m$. This is perhaps the more likely explanation. At the same time, it is possible that more profound alteration occurs in the electron microscope, causing not only shrinkage along c but also doubling of b and alteration in space-group. In this case the X-ray results give the true cell for unaltered material and the true space-group is possibly $P2/a$.

Relations between rhodesite, mountainite, and the zeolites. Mountain

drew attention to the close similarity of rhodesite in many of its properties to the fibrous zeolites, and showed that this similarity extended to ready loss and recovery of the greater part of the water. A similar resemblance exists with mountainite, which shows a close crystallographic relation to thomsonite and gonnardite (M. H. Hey, 1932; H. Meixner, M. H. Hey, and A. A. Moss, 1956). Resemblances include the fibrous habit; the optical properties; the fibre-repeat or pseudo-repeat distance; the approximate values and equality of the other two axes; the number of oxygen atoms (80) and of water molecules (24) in the unit cell; and the apparent ability of Na, K, and Ca to deputize for each other in cation

TABLE IV. Correlation of the unit-cell parameters (Å.) for rhodesite and mountainite.

Rhodesite.		Mountainite.	
c 14·1	(7·05)	*b* 13·10	(6·55)
b 13·1	(6·54)	*a* 13·51	
a 23·8		*c* 13·51	

positions. Differences include the absence of alumina in mountainite; the crystal system, which is orthorhombic in thomsonite; the number of cations in the cell (over 20 in mountainite, usually near 12 in thomsonite); and the greater effect of heating at 275° C. with mountainite. Thomsonite suffers only minor lattice shrinkage at this temperature (Hey, 1932).

Although no such close crystallographic relationship has been traced between rhodesite and any particular zeolite, the general similarity to the fibrous zeolites is apparent. There is also a marked resemblance to mountainite in the unit-cell contents, which are just half as great, except for a small difference in water contents. The unit-cell parameters may also be related. They are correlated in table IV with respect to their fibre axes and cleavage planes. The true cell of rhodesite is assumed to have doubled values for *b* and *c* (in accordance with the super-lattice reflections found in some of the electron-diffraction patterns), and the pseudo-cell parameters are shown in brackets.

The parameters are comparable in the cleavage planes of the two minerals, while the other parameter is roughly twice as great for rhodesite as for mountainite. The degree of order in rhodesite has been shown to be variable, and it is possible that the structures of the two minerals are closely related, but have slight distortions and differences of atomic contents that necessitate the selection of rather different axes and parameters.

In the absence of more complete structural studies, only a tentative explanation is possible of the similarity of rhodesite and mountainite to

the fibrous zeolites. In the latter there are three-dimensional anionic frameworks of empirical composition $(Si,Al)O_2$, on which a negative charge arises from replacement of silicon by aluminium. Rhodesite and mountainite may possibly have incomplete anionic frameworks, derived from those of fibrous zeolites by the absence of one-fifth of the tetrahedral atoms. Such frameworks would bear a negative charge, even though no aluminium were present, because some of its oxygen atoms would be linked to only one silicon atom. The empty tetrahedral sites probably occur in regular and not random positions, because the unit cell of mountainite differs from that of thomsonite in symmetry as well as in size. The reduction in the number of tetrahedral atoms apparently makes room for an increased number of cations.

Dehydration. The present results show that the unit cell of rhodesite is substantially unaltered after heating at 500° C., while Mountain's results show that all the water is lost, to a large extent reversibly, by 275° C. Mountainite is less stable to heat, loss of the water in this case being accompanied or followed by collapse of the structure. Both kinds of behaviour are known among zeolites.

The differential thermal analysis curves (fig. 5) of the two minerals are closely similar to each other, but differ markedly from that of thomsonite. The endothermic peaks at 332–45° C. are probably caused by dehydration, and those at 735° C. by melting. The first endothermic peaks differ slightly in shape and in position for the two minerals. There is a slight exothermic bulge at 375° C. with mountainite, but not with rhodesite; it may be associated with the structural collapse already mentioned. Mountainite shows only a slight exothermic bulge at 960° C., but with rhodesite there is a distinct peak. This possibly corresponds with the transition from β- to α-$CaSiO_3$ as the X-ray results show that this probably occurs below 1000° C. in the partly devitrified glass formed from rhodesite. As both minerals melt well below this temperature, the difference between them in this respect must be attributed to the minor differences in composition and not to the differences in structure.

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Heating experiments on some natural titaniferous magnetites.

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Summary. Chemically analysed samples of magnetites carrying exsolved ulvöspinel and ilmenite have been heated *in vacuo* at various temperatures without change in overall chemical composition and the changes occurring studied microscopically, magnetically, and by X-rays.

Magnetite with exsolution bodies of ulvöspinel can be homogenized probably below 600° C.; thermomagnetic curves and microscopic textures suggest that the solvus curve is very steep at the Fe_3O_4 end of the Fe_3O_4–Fe_2TiO_4 series.

On heating magnetite containing ilmenite lamellae up to 950° C., some interchange of ions between the phases occurs ($Fe_3O_4 + FeTiO_3 \rightarrow Fe_2TiO_4 + Fe_2O_3$), the ilmenite lamellae taking Fe_2O_3 into solid solution. The accompanying host magnetite not only gains Fe_2TiO_4, but at the same time dissolves some $FeTiO_3$. Above 950° C. extensive decomposition takes place, with the production of pseudobrookite, and homogenization has not been achieved. It is suggested that under magmatic conditions extensive solid solution exists in which the $FeTiO_3$ component may be regarded as having a spinel (γ) structure; after exsolution, monotropic inversion may occur to yield a rhombohedral ferri-ilmenite (Chevallier *et al.*, 1955), which on slow cooling changes in composition towards $FeTiO_3$.

Magnetite with exsolution bodies of both ulvöspinel and ilmenite shows on heating the features of both the above binary types.

THERE is still a lack of precise information concerning the solid solution relationships and unmixing of the various phases in the Fe–Ti–O system, including the important part involving magnetite, ulvöspinel, ilmenite, and hematite. A thorough knowledge of the behaviour of complex titanomagnetite solid solutions on cooling would be of great interest not only petrogenetically but also to the geophysicist, since these materials are the principal carriers of rock magnetism.

In previous papers (Vincent and Phillips, 1954; Chevallier, Mathieu, and Vincent, 1954) we have discussed relationships between bulk chemical composition, unmixing intergrowths, and simple magnetic properties of some Fe–Ti oxide minerals from the Skaergaard gabbroic intrusion,

and indicated how the chemical composition of the titanomagnetites and hence the mineralogical nature of the intergrowths produced on their slow cooling might depend rather delicately upon oxidation-reduction relationships between oxide minerals and magmatic liquids.

In the absence, so far, of any published detailed synthetic investigation of the Fe–Ti–O system, we have performed simple heating experiments with a few carefully selected, purified, and chemically analysed natural titaniferous magnetite intergrowths to see how the process of partial or complete homogenization varies with mineralogical and hence chemical composition. This in turn may allow us to predict some of the changes that will occur as a titanomagnetite crystallizes and cools in a magma.

The mineralogical changes occurring during these heating experiments were followed microscopically and by determining the changes in unit-cell dimensions of the various phases, and also by quantitative measurements of their magnetic properties. The magnetic measurements have been made by Chevallier and Mathieu at Nancy, the rest of the work has been done by Vincent and Wright at Oxford. The interpretation of the results has been done jointly, and one of us (E.A.V.) has been responsible for preparing this paper.

A fairly detailed study of this kind seems justified in view of such compilations of partial chemical analyses, X-ray, and magnetic data for titaniferous magnetites as those presented by Akimoto (1954, 1955) in which correlation between these various properties is often far from good, since the discrepancies may be partly explicable if the minerals described have unmixed to varying extents and in different ways according to their composition.

The majority of the unmixed titaniferous magnetites found in igneous rocks consist of cubic magnetite carrying exsolution lamellae of rhombohedral ilmenite arranged along the {111} directions of the host spinel; others carry both ilmenite and ulvöspinel in various proportions as exsolution bodies; while others—apparently rather few in coarse-grained rocks—carry only ulvöspinel. Homogeneous titanomagnetites of this last type (solid solutions along the Fe_3O_4–Fe_2TiO_4 binary join) have been synthesized by Pouillard and Michel (1949) and by Kawai, Kume, and Sasajima (1954); the latter authors prepared an extreme solid solution with 80 % Fe_2TiO_4. Solid solutions in the binary join Fe_3O_4–$FeTiO_3$ were synthesized by Chevallier and Girard (1950) with compositions ranging from pure Fe_3O_4 up to 37 % $FeTiO_3$; these materials also all gave the spinel X-ray powder pattern.

The crystalline structures of these two distinct series of solid solutions have been discussed by Chevallier, Bolfa, and Mathieu (1955), who refer to them as titanomagnetites types I and II respectively. We have found that the behaviour of our natural unmixed intergrowths on heating *in vacuo* is quite different in the two binary series, while samples of intermediate composition show features of both types.

Various authors have previously given brief descriptions of heating experiments carried out on titaniferous magnetites, generally with a view to demonstrating the lamellae of ilmenite parallel to {111} to be of exsolution rather than of replacement origin. Among these may be mentioned Ramdohr (1926), Kamiyama (1929), Wilson (1953), and Roy (1954, 1955). In none of these experiments have carefully separated and chemically analysed materials been used; neither have any quantitative measurements been made of changes occurring in cell-dimensions or magnetic constants on heating. Mogensen (1946), however, reported the homogenization of the first magnetite–ulvöspinel intergrowth to be described in the literature by heat treatment at 600° C. *in vacuo*, to yield a spinel with $a = 8{\cdot}43$ Å.

Materials and methods.

Titaniferous magnetites from coarse-grained igneous rocks were chosen for the present work, mainly because the exsolution of the various phases is complete or nearly so in such materials, which represent a close approach to the attainment of equilibrium conditions during crystallization and subsequent cooling.

Detailed experiments have been carried out with four samples, and a few observations made with five others. Three of the samples (designated C.S.L. 2, 3, and 5) are from titaniferous magnetite bodies (associated with Precambrian anorthosites) at Schmoo Lake, near Lac la Blache, Comté du Saguenay, Quebec, Canada, kindly provided by Dr. J. P. Girault, who has already published a brief description of them (Girault, 1953), while the remainder (designated by E.G. nos.) are from the Skaergaard intrusion, East Greenland, kindly provided by Prof. L. R. Wager.

The magnetites for study were selected first on the basis of microscopic examination, and practically pure samples (better than 99·5 % as checked microscopically) of grains passing 120-mesh bolting cloth were prepared chiefly by means of an A.C. electromagnet and simple elutriation.

Complete chemical analyses were made (table I), the overall compositions of the materials being plotted on the conventional Fe–Ti oxide triangular diagram (fig. 1), in which MgO, MnO, and CaO are added to

TABLE I. Chemical analyses of titaniferous magnetites.

Analysis no.		1.	2.	3.	4.	5.	6.	7.	8.	9.
Sample no.		E.G. 2308.	C.S.L. 2.	E.G. 4359.	E.G. 2569.	C.S.L. 3.	E.G. 4355.	C.S.L. 5.	E.G. 4353.	E.G. 4430.
Weight %										
MO	FeO	46·06	45·04	34·13	41·09	43·36	40·11	33·79	39·8	36·6
	MgO	2·29	3·61	1·84	1·05	2·58	2·34	1·49	0·9*	0·5*
	MnO	0·33	0·36	0·37	0·45	0·40	0·37	0·28	0·4*	0·4*
	CaO	0·06	0·13	0·49	0·15	0·20	0·40	0·20	0·7	0·7
R_2O_3	Fe_2O_3	28·37	25·82	40·70	32·38	29·28	36·86	51·68	36·8	41·7
	Al_2O_3	1·39	2·70	2·54	2·98	2·28	2·77	2·91	3·1*	2·7*
	V_2O_3	1·97	0·42	1·52	0·40	0·48	0·64	0·58	2·1*	1·1*
	Cr_2O_3	0·07	0·26	0·03	0·00	0·22	0·05	0·13	—*	—*
TO_2	TiO_2	19·42	21·87	18·55	21·17	21·31	16·56	9·36	15·6	15·3
	SiO_2	0·10	0·04	0·05	n.d.	0·03	0·08	0·05	0·1*	0·2*
Total		100·06	100·25	100·22	99·67	100·14	100·18	100·47	99·5	99·2
Molecular proportions										
MO		61·0	60·8	50·6	54·8	58·6	57·1	52·0	55·6	52·5
R_2O_3		17·8	16·2	27·4	21·2	18·2	23·9	36·1	25·9	28·6
TO_2		21·2	23·0	22·0	24·0	23·2	19·0	11·9	18·5	18·9

Analysts: E. A. Vincent and J. B. Wright. Spectrographic determinations (*) in nos. 8 and 9 by S. R. Taylor.

Note: The analyses given above for E.G. 2308 and E.G. 2569 refer to completely new samples of these magnetites (in the case of E.G. 2569 separated from a different hand specimen), and differ slightly from those previously published (Vincent and Phillips, 1954, table 2) under the same sample numbers.

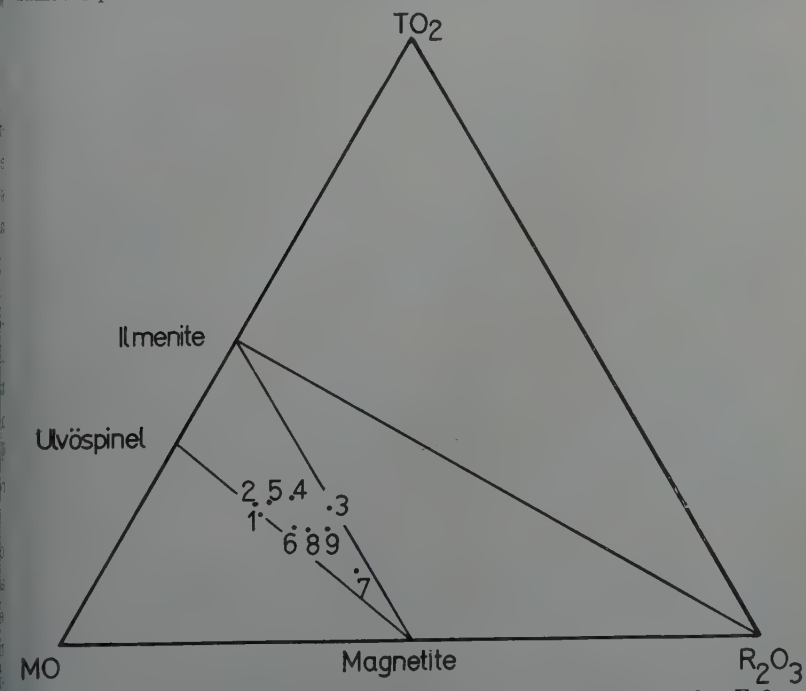


FIG. 1. Molecular composition of analysed titaniferous magnetites. $MO = FeO + MgO + MnO + CaO$; $R_2O_3 = Fe_2O_3 + Al_2O_3 + V_2O_3 + Cr_2O_3$; $TO_2 = TiO_2 + SiO_2$. The numbers refer to analyses in table I.

FeO; Al_2O_3, Cr_2O_3, and V_2O_3 are added to Fe_2O_3; and SiO_2 is added to TiO_2. Two of the titaniferous magnetites studied in some detail (C.S.L. 2 and E.G. 2308) lie almost precisely in the Fe_3O_4–Fe_2TiO_4 binary join; a

TABLE II. Normative compositions of titaniferous magnetites.

	1. E.G. 2308.	2. C.S.L. 2.	3. E.G. 4359.	4. E.G. 2569.	5. C.S.L. 3.	6. E.G. 4355.	7. C.S.L. 5.	8. E.G. 4353.	9. E.G. 4430.
Weight %:									
Magnetite, &c.									
$FeO.Fe_2O_3$ ...	37·43	32·34	52·36	44·42	37·80	47·37	68·12	50·3	57·6
$MgO.Fe_2O_3$ ...	2·86	3·99	4·33	1·75	3·46	4·25	4·64	1·8	1·2
$MnO.Fe_2O_3$ ...	0·28	0·25	0·58	0·48	0·35	0·44	0·55	0·5	0·7
$CaO.Fe_2O_3$ ...	0·06	0·11	0·88	0·19	0·22	0·56	0·50	0·9	1·1
$FeO.Al_2O_3$ ...	2·15	3·99	3·83	4·80	3·48	4·20	4·50	4·9	4·4
$MgO.Al_2O_3$ ...	0·16	0·47	0·30	0·17	0·30	0·36	0·28	0·1	0·1
$MnO.Al_2O_3$ ...	0·02	0·03	0·03	0·05	0·03	0·03	0·03	0·2	—
$CaO.Al_2O_3$ ...	—	0·02	0·06	0·02	0·02	0·05	0·03		—
$FeO.V_2O_3$ ...	2·64	0·53	2·00	0·55	0·64	0·84	0·80	2·9	1·6
$MgO.V_2O_3$ ...	0·21	0·06	0·17	0·02	0·06	0·08	0·06	0·2	—
$MnO.V_2O_3$ ...	0·02	—	0·02	—	—	0·02	—	—	—
$CaO.V_2O_3$ ...	—	—	0·02	—	—	—	—	—	—
$FeO.Cr_2O_3$ ...	0·09	0·34	0·04	—	0·27	0·07	0·18	—	—
$MgO.Cr_2O_3$ ...	—	0·04	—	—	0·02	—	0·02	—	—
	45·92	42·17	64·62	52·45	46·65	58·27	79·71	61·8	66·7
Ulvöspinel, &c.									
$2FeO.TiO_2$ ...	49·82	49·59	2·26	22·66	39·64	31·17	8·12	24·9	10·9
$2MgO.TiO_2$ ...	3·18	5·09	0·16	0·74	3·02	2·32	0·47	0·6	0·2
$2MnO.TiO_2$ ...	0·35	0·40	0·02	0·24	0·38	0·29	0·07	0·8	0·2
$2CaO.TiO_2$ ...	0·08	0·15	0·04	0·10	0·21	0·35	0·06		0·2
	53·43	55·23	2·48	23·74	43·25	34·13	8·72	26·3	11·5
Ilmenite, &c.									
$FeO.TiO_2$ ...	—	2·31	29·83	22·65	9·19	6·90	10·74	11·2	20·7
$MgO.TiO_2$ ...	—	0·26	2·26	0·82	0·77	0·56	0·67	0·3	0·5
$MnO.TiO_2$ ...	—	0·02	0·32	0·24	0·09	0·06	0·09	0·3	0·2
$CaO.TiO_2$ ...	—	0·01	0·49	0·10	0·05	0·08	0·07		0·4
	—	2·60	32·90	23·81	10·10	7·60	11·57	11·8	21·8
Excess *MO* group	0·65	—	—	—	—	—	—	—	—
Limiting weight:									
% of Fe_3O_4 ...	41·13	37·44	59·01	46·95	42·45	53·44	74·93	53·4	60·46
Molecular percentages:									
Magnetite, &c. ...	44·62	41·24	55·45	46·95	44·02	55·72	75·16	58·3	60·2
Ulvöspinel, &c. ...	53·34	54·97	2·18	21·46	41·74	33·39	8·42	25·2	10·5
Ilmenite, &c. ...	—	3·79	42·37	31·59	14·24	10·89	16·42	16·5	29·3
Excess *MO* group	2·04	—	—	—	—	—	—	—	—

third, E.G. 4359, lies almost precisely in the Fe_3O_4–$FeTiO_3$ binary join; while the fourth, E.G. 2569, lies in the field between the two principal series.

Normative mineralogical compositions have been calculated from the analyses (table II), the present norms (devised by Chevallier) differing from those previously published by one of us (Vincent and Phillips, 1954)

in that redistribution of the oxide molecules of the analysis is now made strictly according to their various molecular proportions, and not so arbitrarily. For instance, we assume that all the sesquioxides of the analysis enter into spinels of the type $MO.R_2O_3$. The group MO comprises FeO, MgO, MnO, and CaO in various proportions, while R_2O_3 comprises Fe_2O_3, Al_2O_3, V_2O_3, and Cr_2O_3. We calculate the fraction of molecules of the MO group that consists of FeO, and we combine this fraction with each of the R_2O_3 type molecules in turn, repeating the process with MgO, MnO, and CaO, until all the R_2O_3 group is combined with MO in spinel molecules. MO remaining is then similarly combined with TO_2 (TiO_2+SiO_2) by means of simultaneous equations in appropriate amounts to balance in the molecules $2MO.TO_2$ (ulvöspinel) and $MO.TO_2$ (ilmenite). The various constituents of the MO group are allotted proportionally in the same way as before.

Since our measurements of magnetic constants are on a weight basis, a detailed weight percentage norm, rounded off to 100 %, is given in table II as well as the totals of the main mineralogical groups in the molecular percentage norm. The table also gives a 'limiting' weight percentage of Fe_3O_4 for each sample, which would apply if all Fe_2O_3 in the analysis were present in the Fe_3O_4 molecule, which is probably the case in the materials that have been completely homogenized by heating.

For the heating experiments at temperatures up to 950° C. about 100 mg. portions of the purified samples were sealed under vacuum (around 10^{-5} cm. Hg) in transparent silica ampoules, with as little free space as possible. The ampoules were packed in sand in crucibles, placed in an ordinary muffle furnace with temperature control and pyrometer, and after heating for the required time were quenched by dropping into a dish of mercury.

The FeO contents of the heated samples were redetermined, showing in all cases that no significant oxidation or reduction had taken place under the simple experimental conditions adopted.

Small portions of the heated grains were mounted in a transparent cold-setting resin and polished for microscopic examination by reflected light.

Detailed X-ray investigation of the materials has not so far been attempted, but the lattice parameters of some critical samples, before and after heating, were measured by means of a Geiger-counter diffractometer, using filtered iron radiation.

Samples of unheated and heated grains were examined magnetically at Nancy, the constants determined being the value of the specific

saturation magnetization (per gram) of the sample at room temperature ($\sigma'_{\infty \cdot 20^\circ \text{C.}}$), and the Curie point ($\theta^\circ$ C.). The symbol σ_∞ is reserved to denote the specific saturation magnetization (per gram) of a *homogeneous* titanomagnetite solid solution, and is used in this sense later in the paper. The methods used have been described previously (Chevallier and Pierre, 1932; Chevallier and Mathieu, 1943; Chevallier, Bolfa, and Mathieu, 1955). The Curie temperature is derived from a photographic record of the change in magnetic moment of the sample with temperature, made with a thermomagnetic balance in a fairly small field. The profiles of these thermomagnetic curves can be analysed only qualitatively, but the Curie temperatures, where sharp, can be estimated with some accuracy.

Magnetite–ulvöspinel intergrowths.

These are structurally the simplest type of unmixed titaniferous magnetite, both phases being inverse spinels, and may be expected to show the simplest relationships during homogenization.

The two samples studied that lie to all intents and purposes in this binary series (E.G. 2308 and C.S.L. 2) are very similar in bulk chemical composition (tables I and II; fig. 1). Normative recalculation shows a slight excess of the *M*O group in E.G. 2308, and a slight excess of ilmenite in C.S.L. 2. Under the microscope both samples are seen at high magnification in oil to consist of a cloth-like intergrowth of magnetite and ulvöspinel, the ulvöspinel being arranged roughly parallel to {100} and {110} of the magnetite. In both samples a very occasional fine lamella (parallel {111}) or granule of ilmenite enclosed in the magnetite is visible. Irregular spindles of a transparent spinel, also arranged parallel to the cube face of the magnetite, are quite abundant in C.S.L. 2, but are not seen in E.G. 2308. They are often enclosed within the 'boxes' formed by the ulvöspinel lamellae, possibly indicating exsolution at an earlier stage in the cooling of the mineral.

The chief difference between the two samples lies in the size of the exsolution bodies of ulvöspinel. The intergrowth is very clearly visible at a magnification of about $\times 1000$ in C.S.L. 2, where it is exceptionally coarse, the rough lamellae of ulvöspinel being around 1 to 2 μ in width (fig. 2), while in E.G. 2308 the scale is finer, individual lamellae measuring 0·25 μ in average width.

The changes in texture on heating at various temperatures are shown for C.S.L. 2 in fig. 2; although the re-solution proceeds rather more readily in the finer-grained E.G. 2308, it was found impossible to

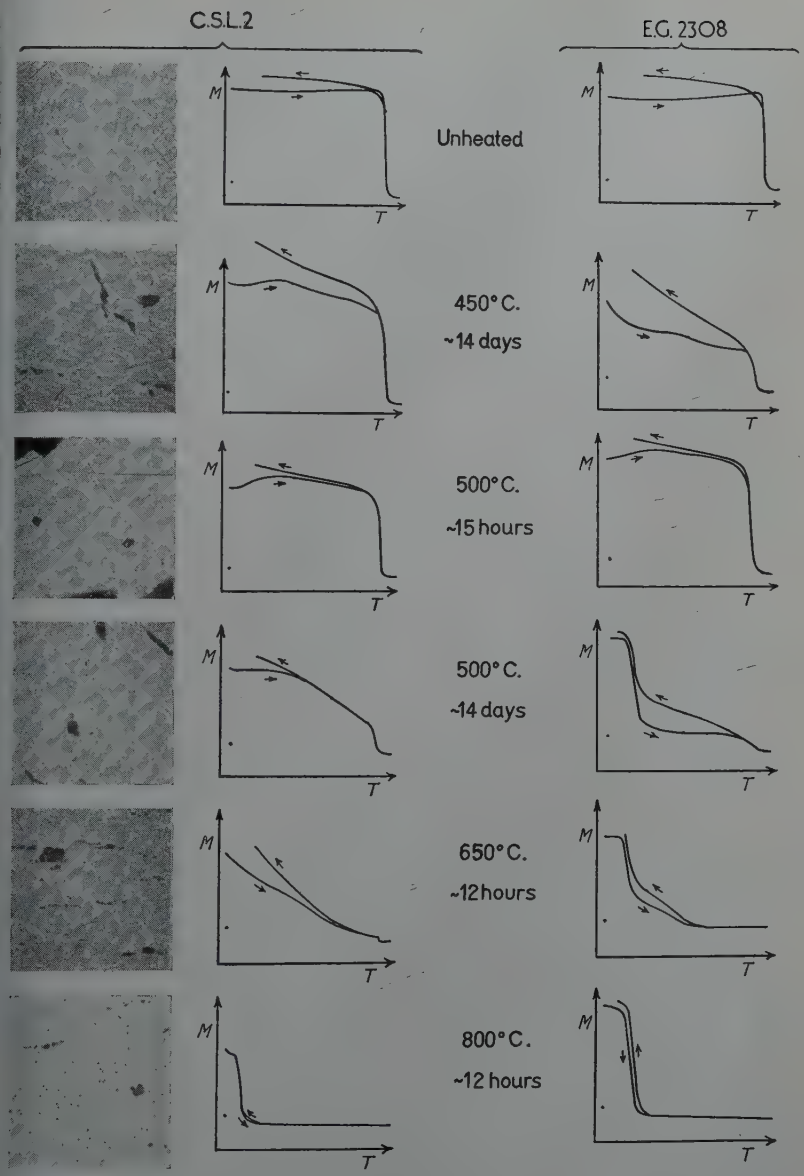
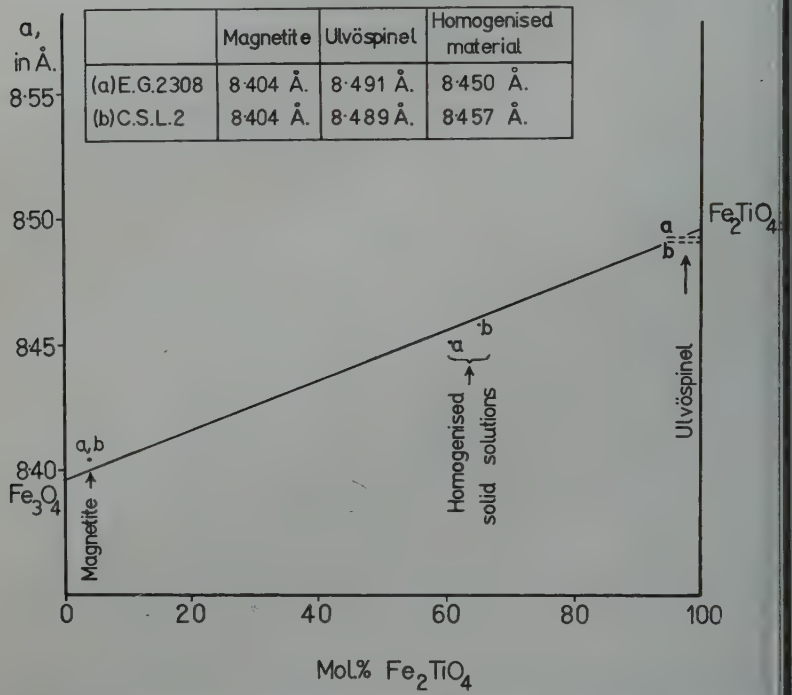


FIG. 2. Photomicrographs (×420, reflected light) and tracings of thermomagnetic curves of heated magnetite–ulvöspinel intergrowths.

produce satisfactory photomicrographs of the latter. The changes observed microscopically in both samples are, however, identical.

Heating for 15 hours at 500° C. causes little observable change, but heating for 14 days at 450° C. causes a general softening of the appearance of the intergrowth, and the areas of the darker ulvöspinel can be



	Magnetite	Ulvöspinel	Homogenised material
(a) E.G.2308	8·404 Å.	8·491 Å.	8·450 Å.
(b) C.S.L.2	8·404 Å.	8·489 Å.	8·457 Å.

FIG. 3. Cell-dimensions of unheated and heated magnetite–ulvöspinel intergrowths

seen to have grown slightly at the expense of the lighter magnetite. This continues on heating at 500° C. for 14 days, and at 550° C. and 650° C. for 12–17 hours. After heating at 800° C. for 12 hours, mutual solution of the magnetite and ulvöspinel can be seen to be complete, although rods of transparent spinel remain; these latter mostly disappear after treatment for 16 hours at 950° C.

The unit-cell dimensions determined for the unheated and homogenized samples are shown in fig. 3. The diffraction peaks measured on the unheated samples are broadened, particularly in the case of ulvöspinel, probably owing to strains set up in the lattices during the original separation of the mineral into two phases. The homogenized

samples yield quite sharp peaks, so that the probable error of the cell-edge determination in these cases is less than ±0·001 Å.; in the case of the phases before heating, where the diffraction profiles had to be analysed geometrically to find the true position of the $K\alpha_1$ peak, the probable error for the magnetite is about ±0·002 Å., for ulvöspinel ±0·005 Å.

The compositions of the samples plotted in fig. 3 require explanation. The measured Curie points for the unheated samples are a little lower than for pure magnetite, indicating that about 4 % of some material remains in solid solution; this material seems most likely to be ulvöspinel. The compositions of the homogenized solid solutions are taken as the molecular proportions of Fe_3O_4 and Fe_2TiO_4 appearing in the normative recalculation of the analyses, reduced to a percentage and ignoring other molecules appearing in the norm. The ulvöspinel phase in fig. 3 has been indicated with a broken line near 100 % Fe_2TiO_4, since it almost certainly in its turn contains some Fe_3O_4 in solid solution; in view of the chemical complexity of the samples, an attempt to calculate the composition of the ulvöspinel phase more precisely might be misleading. A straight line has been drawn between 8·396 Å., the cell edge for pure magnetite as determined by Basta (1953), and 8·495 Å., the mean of the values given for Fe_2TiO_4 by Barth and Posnjak (1932; 8·50 Å.) and by Ernst (1943; 8·49 Å.). Our determinations for unheated and homogenized materials fall fairly close to this line, indicating agreement with Végard's mixture law.

Our cell-dimensions for the magnetite phases of both unheated samples are rather larger than that of pure magnetite; this could be due to some Fe_2TiO_4 remaining in solid solution. Our values for ulvöspinel are in close agreement with those of Ernst and of Barth and Posnjak for synthetic material, and lower than Pouillard's (1950) value of 8·534 Å. It may be noted that Pouillard's value for magnetite (8·413 Å.) is also high (see also Nicholls, 1955, p. 132). Precise correlation between cell-dimensions and compositions of our samples is hardly to be expected, since the manner of distribution of ions other than Fe'', Fe''', and Ti^{IV} in the various lattices cannot be determined; this is the reason why we have adopted a form of normative recalculation of the analyses in which the minor elements are not assigned preferentially to any particular phase.

For each heated sample the saturation magnetization has been measured and a thermomagnetic curve recorded. Accurate tracings of some of the latter are reproduced in fig. 2. In each diagram the ordinate represents a non-linear scale of magnetic moment (not necessarily

precisely the same for each sample) and the abscissa the temperature scale. The spot in each tracing marks the position of the light spot of the thermomagnetic balance (Chevallier *et al.*, 1955, p. 357) before the sample was heated: it thus represents a temperature of about 20° C. The far ends of the traces represent a temperature of 620° C. Small arrows indicate the profiles of the thermomagnetic curves obtained on heating and then cooling the samples; the traces for temperatures below the Curie point are generally not coincident, due to thermoremanence.

TABLE III. Magnetite-ulvöspinel intergrowths: magnetic constants of heated samples. σ'_∞ is given for 20° C., in electromagnetic units per gram.

Heated, ° C.	Original sample	450	450	450	500	500	545	650	800	950
hrs.	(unheated)	12	336	504	15	336	12	12	12	16
C.S.L. 2										
θ° C.	563	562	558	—	557	550	—	*	80	80
σ'_∞	32·8	28·8	21·3	—	21·2	17·0	—	16·4	17·8	17·2
E.G. 2308										
θ° C.	562	550	546	550	552	*	*	*	130	130
σ'_∞	35·0	30·3	21·5	21·4	21·3	23·1	23·0	23·1	22·4	21·9

* indicates that the heated sample did not show a sharp Curie point.

The thermomagnetic curves of the unheated samples show a sharp Curie point at 563° C. (fig. 2; table III). Using the curve constructed by Chevallier *et al.* (1955, p. 364), relating Fe_3O_4 content with Curie point in homogeneous titanomagnetites, we may deduce that the magnetic spinel phase of the unheated complex titaniferous magnetite contains about 96 % Fe_3O_4, the 4 % of material remaining in solid solution being probably ulvöspinel (Chevallier, Mathieu, and Vincent, 1954, pp. 30–31).

In samples heat-treated at temperatures up to 500° C. there is little change in the Curie point, which falls only to around 550° C. as can be seen from the curves in fig. 2. The *composition* of the ferromagnetic spinel phase thus changes but little on heating at moderate temperatures; the slight lowering of the Curie point indicates that about 3 % more ulvöspinel re-enters into solid solution.

The specific saturation magnetization (σ'_∞) is also a direct function of the Fe_3O_4 content in a homogeneous ferromagnetic spinel phase (Chevallier *et al.*, 1955, pp. 360–1). This parameter, unlike the Curie point, falls rapidly in the early stages of the heating process and then attains a constant value[1] (table III). Since the composition of the mag-

[1] A physical explanation of this phenomenon will be given in a further paper in the course of preparation by R. Chevallier.

netic phase changes very little at first, this initial drop in the saturation magnetization indicates a decrease in the *quantity* of the magnetic phase, which thus clearly begins to redissolve in the ulvöspinel, even at 450° C., the lowest temperature at which we have made experiments.

The thermomagnetic curves of C.S.L. 2 show the persistence of a limiting Curie point at about 550° C. in samples heated up to 650° C.; in E.G. 2308 up to 550° C. The profiles of the curves change steadily, however, and the presence in the samples of grains in varying stages of homogenization gives rise to long sloping portions on the traces (fig. 2). Changes in the profiles are seen more clearly and at lower temperatures of heating in E.G. 2308 than in C.S.L. 2; this is because the intergrowth of magnetite and ulvöspinel is very much finer in the former material, so that homogenization proceeds more rapidly. The equivalent effects of time and of temperature in the homogenization process are clearly shown by the curves for E.G. 2308 heated for 14 days at 500° C., and for 12 hours at 550° C. (not shown in fig. 2) which are practically identical, and not very different from that for 12 hours heating at 650° C. Further, the changes in thermomagnetic curve and in microscopic texture in samples of both materials heated at 500° C. first for 15 hours and then for 14 days are most striking.

The curve of E.G. 2308 heated for 14 days at 500° C. (fig. 2), while still showing a remnant of the original high Curie point, also shows clearly the low Curie point of the final solid solution; the thermomagnetic curve for a further sample heated for 3 weeks at 525° C. shows it to be sensibly homogeneous. If heated for long enough, even at 450°, the material would probably yield a curve identical with that of the samples heated at 800° C. and 950° C., where there is a single sharp Curie point at 130° C., representing the final spinel solid solution. C.S.L. 2 behaves similarly, but the homogenization proceeds more slowly.

The profiles of the thermomagnetic curves thus lend graphic expression to the process of homogenization in the Fe_3O_4–Fe_2TiO_4 series. We may envisage that, as heating progresses, magnetite begins to dissolve in the ulvöspinel without itself taking much Fe_2TiO_4 into solid solution. A more or less heterogeneous mixture is thus formed, the Curie points of individual grains in which vary between that of magnetite and that of the final metastable solid solution. As long as any of the initial magnetite is left, the drop at 550° C. in the thermomagnetic curve will persist; when the last of the magnetite is dissolved this drop disappears; then, as the solid solutions in the various grains approach homogeneity,

the residual part of the curve gradually vanishes and we are finally left with the sharp drop of the final homogeneous solution.

The possible form of solvus in the Fe_3O_4–Fe_2TiO_4 binary system has been discussed by Phillips (Vincent and Phillips, 1954) who, from an examination of microscopic textures, considers that magnetite and ulvöspinel probably form a sub-solidus eutectic; and by Kawai, Kume, and Sasajima (1954) and Kawai (1956), who, on the basis of some heating experiments and magnetic measurements, propose a simple hoop-shaped unmixing curve of the type found in the alkali felspars. The present authors consider there is no real evidence for a eutectic, and prefer for the present to accept the interpretation of the Japanese workers.

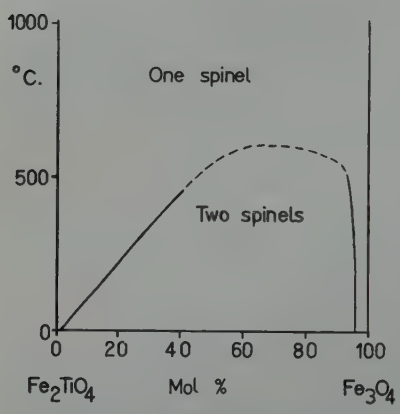


FIG. 4. Possible form of the solvus in the Fe_3O_4–Fe_2TiO_4 binary series.

Our clear observation, from magnetic measurements and microscopic examination, that magnetite dissolves in ulvöspinel on heating without itself taking much ulvöspinel into solution, leads us to modify somewhat the shape of curve from that proposed by Kawai *et al.* In fig. 4 the limb of the solvus at the Fe_3O_4 end of the diagram leaves the composition abscissa at about 96 % Fe_3O_4 (θ = 563° C.) at room temperature and rises steeply, passing through 93 % Fe_3O_4 (θ = 550°) at about 500° C. The other limb of the curve is also drawn starting a little on the Fe_3O_4 side of pure Fe_2TiO_4: we have no direct evidence for this, except perhaps the very slightly lower cell-dimensions of our ulvöspinel as compared with published values for the pure synthetic material. Kawai *et al.* (1954) put the crest of their solvus at about 37 mol. % Fe_2TiO_4 and 750° C.; Kawai's (1956) diagram shows the crest temperature at 600° C., but he does not comment on this discrepancy. In fig. 4 we have adopted Kawai's later value. The two materials we have investigated both contain around 60–65 mol. % Fe_2TiO_4 and 40–35 mol. % Fe_3O_4 (ignoring minor constituents) and would almost certainly homogenize completely at about 450° C., if heated long enough. The solvus limb has therefore been sketched to pass through a temperature of about 450° C. at this composition.

A sample of C.S.L. 2, previously homogenized by heating at 800° C., was subsequently held at 300° C. for 6 weeks, to see whether any unmixing of the magnetite and ulvöspinel phases could be brought about. However, no significant change could be observed in the magnetic constants after this treatment, and X-ray diffractometer measurements confirmed that no unmixing whatever had taken place.

Magnetite–ilmenite intergrowths.

Only one sample (E.G. 4359) falling practically in the magnetite–ilmenite binary series has been studied in detail (analysis no. 3 in tables I and II and fig. 1).

This particular intergrowth of magnetite and ilmenite is on an extremely fine scale for the most part (fig. 5) and details of the texture are difficult to resolve with the microscope even at the highest magnifications. The majority of grains only carry ilmenite lamellae of such minute width that individual lamellae are not easily discernible, but a few of the magnetite grains also carry relatively broad ilmenite lamellae arranged along the usual octahedral directions. The reason for exsolution of ilmenite on such a fine scale in some magnetites is not entirely clear; it may sometimes be a matter of rapid cooling, or sometimes a matter of direct oxidation from already exsolved ulvöspinel (see also Ramdohr, 1953). In any event it is interesting to note in passing that such finely exsolved ilmenite in magnetite is a feature observed in most of the Skaergaard Middle Gabbros so far examined—rocks in which textural and other mineralogical evidence does not necessarily imply rapid cooling (see, for example, Brown, 1957). The magnetite grains of E.G. 4359 also carry myriads of minute transparent spinel grains, evenly distributed except where they form a beaded edge to large ilmenite lamellae. Their total bulk relative to the magnetite is small.

E.G. 4359 was selected for heating experiments because it was thought that its very fine scale of exsolution might facilitate the attainment of homogenization; this proved not to be the case, and its behaviour on heating is totally different from that of the magnetite–ulvöspinel intergrowths described above. Little or no change in the texture was discernible in samples heated at temperatures up to 600° C. for 12 hours. A sample heated for 12 hours at 750° C., however, showed that the rhombohedral lamellae had increased in width and organization, now showing clearly their relation to the octahedral planes of the magnetite (fig. 5). At the same time the reflectivity of the lamellae increased and they appeared whiter, though retaining reflection pleochroism; the magnetite,

E.G.4359

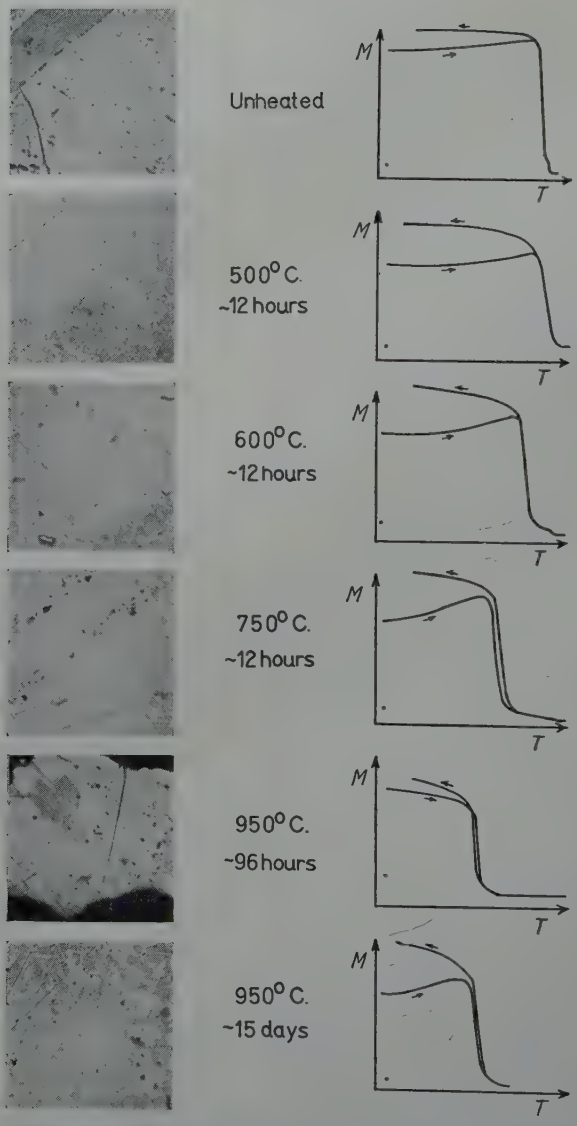


FIG. 5. Photomicrographs (× 420, reflected light) and tracings of thermomagnet curves of heated magnetite–ilmenite intergrowth E.G. 4359. (The photomicrogra of a grain heated for 96 hours at 950° C. shows the very rare development of (darke pseudobrookite at the expense of portions of the ferri-ilmenite lamellae.)

on the contrary, appeared darker in tint. Similar features were observed by Ramdohr (1926) in his experiments with a Taberg magnetite, and interpreted qualitatively (Ramdohr, 1955, p. 137) in terms of migration of Fe_2O_3 from the spinel phase into the rhombohedral lamellae.

A sample of E.G. 4359 heated for 96 hours at 950° C. shows the process to have gone farther, the lamellae decreasing in area and beginning to resemble hematite in appearance. Heating for 3 weeks at 950° C. brought about no change in bulk chemical composition, but still failed to produce a homogeneous solid solution. The authors conclude that a reaction relationship exists between magnetite and ilmenite, so that on heating, the original lamellae of ilmenite change in composition towards hematite, and members of the $FeTiO_3$–Fe_2O_3 series of rhombohedral solid solutions are produced; the X-ray and magnetic measurements also support such an interpretation of the optical changes.

Attempts at homogenizing this sample by heating at high temperatures without change in bulk composition have so far failed. A sample heated at 1250–1300° C. for 5 hours in an evacuated silica ampoule showed slight oxidation; rhombohedral lamellae were still present, and patches of pseudobrookite were developed. Indeed, this latter phase has been observed very occasionally in samples heated at 950° C. for 96 hours, where it has been produced in the lamellae at the expense of the ilmenite–hematite solid solution (fig. 5); Ramdohr (1955, p. 785) has drawn attention to the spontaneous dissociation of ilmenite–hematite materials into pseudobrookite and magnetite on heating above 1100° C. As far as the authors are aware, none of the reports of successful homogenization of magnetite–ilmenite intergrowths in the literature confirm that the bulk composition of the samples remained unchanged.

The measured value of the cube edge of the magnetite component in the original unheated material agrees exactly with Basta's (1953) value for pure natural Fe_3O_4, and is slightly smaller than the values obtained for the magnetite component of the magnetite–ulvöspinel intergrowths described above:

	Magnetic spinel phase.	Non-magnetic rhombohedral phase.		
	a, Å	*a*, Å.	*c*, Å.	*c*/*a*
Unheated sample ...	8·396±0·002	5·088±0·001	14·092±0·002	2·770
Heated 96 hours at 950° C.	8·410±0·001	5·068±0·001	13·92±0·01	2·749

The parameters *a*, *c*, and *c*/*a* (referred to the hexagonal cell) for the

ilmenite lamellae are all higher than the values generally quoted in the literature, of which Basta's (1953; see fig. 6) are typical. Our measurements have been repeated and thoroughly checked, but we can find no

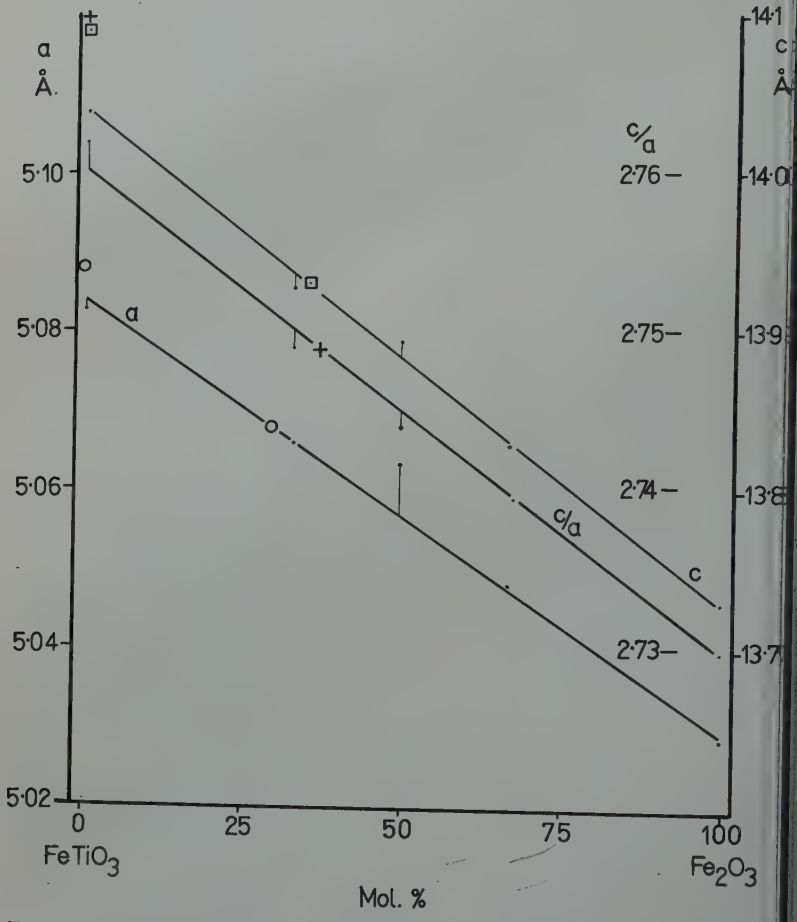


FIG. 6. Basta's (1953) lattice parameters (.) for α-$FeTiO_3$–α-Fe_2O_3 solid solutions. Parameters for rhombohedral phase of E.G. 4359, unheated, and heated for 96 hours at 950° C. inserted: ○ a; ⊡ c; + c/a.

reason to change our values; Dr. R. St. J. Lambert (personal communication) informs us that he has obtained values very similar to ours for an ilmenite containing about 5 % Al_2O_3, but otherwise unremarkable in its composition. A possible reason for our high values might be that

most of the Mg and Mn revealed in the analysis of this ilmenomagnetite is concentrated in the ilmenite lamellae, since $MgTiO_3$ and particularly $MnTiO_3$ are generally reported to have rather larger cell-dimensions than $FeTiO_3$. There is no direct evidence for this, but it was observed previously (Vincent and Phillips, 1954) that these two elements were significantly concentrated in discrete ilmenite crystals as compared with the accompanying ilmenomagnetite in rocks of the Skaergaard intrusion.

After heating for 96 hours at 950° C. the parameters of the rhombohedral phase have all fallen significantly, consistent with the entry of α-Fe_2O_3 into solid solution. Such a decrease in lattice parameters of the rhombohedral component of a heated ilmenomagnetite was also observed by Basta (1953), who further gives values for the cell-dimensions of three solid solutions intermediate between $FeTiO_3$ and α-Fe_2O_3 (quoted in Nicholls, 1955, p. 137). Basta's figures are plotted in fig. 6, where straight lines have been drawn to indicate the approximate variation in parameter with composition. The values of a, c, and c/a for original and heated samples of E.G. 4359 have been added; the parameters for the heated sample have been placed on the straight lines through Basta's points. The compositions of the final rhombohedral solid solution to be deduced from each parameter are in fair agreement, but some of Basta's points in this part of the series are somewhat aberrant (see fig. 6), so that the positions of the lines relating parameters with molecular composition are none too well defined. We may at least say that our observed parameters in the heated sample are consistent with a ferri-ilmenite carrying between 30 and 40 % Fe_2O_3 in solid solution.

We cannot be sure that it is strictly valid to refer our observed lattice parameters to the lines drawn through Basta's points, since our original ilmenite has a larger cell than his. On heating the sample, the reaction $Fe_3O_4 + FeTiO_3 \rightarrow Fe_2O_3 + Fe_2TiO_4$ proceeds to some extent, and it may be that any Mg or Mn replacing Fe″ in the ilmenite tends to react to form an ulvöspinel-type 'molecule' before the iron. In this way, the solid solution with Fe_2O_3 may approach Basta's line more closely as reaction progresses.

The cubic magnetic spinel phase arrived at concurrently on heating for 96 hours at 950° C. gives a value $a = 8{\cdot}410 \pm 0{\cdot}002$ Å. for the cube edge, as against $8{\cdot}396 \pm 0{\cdot}002$ Å. for the unheated material.

Nicholls (1955, p. 149), in the course of an excellent theoretical discussion of the phase-change relationships during unmixing of a homogeneous crystal in the Fe_3O_4–$FeTiO_3$ series, points out that attempts

to rehomogenize magnetite–ilmenite intergrowths are unlikely to succeed because 'the solid solutions from which the intergrowths formed are probably metastable intermediates between magnetite and a cubic form of $FeTiO_3$ (γ-$FeTiO_3$) which cannot be produced by heating rhombohedral $FeTiO_3$ (ilmenite)'. Mason's (1943) discussion of the monotropic nature of the hematite–maghemite inversion should also be borne in mind in this connexion.

The possible existence of a spinellid form of $FeTiO_3$, having a defect lattice structure analogous with that of maghemite, γ-Fe_2O_3, has occurred to various mineralogists interested in the iron–titanium oxides, but only recently have any firm proposals been put forward for its possible structure (Chevallier, Bolfa, and Mathieu, 1955; Nicholls, 1955), and it has not yet been found in nature[1] or prepared synthetically. It may be that γ-$FeTiO_3$ can have no stable independent existence, but may be regarded only as entering into solid solution with magnetite over an extensive compositional range at high temperatures. Chevallier *et al.* and Nicholls discuss its possible structure in view of the magnetic properties of its solid solutions with magnetite, but unfortunately little precise X-ray data are available for such solid solutions. Chevallier and Girard (1950) observed that the cell-dimensions of their synthesized cubic Fe_3O_4–$FeTiO_3$ solid solutions appeared very similar to magnetite up to a composition of 37 mol. % $FeTiO_3$. Basta (1953) gives the value 8·3475 Å. for the cube edge of a titanomaghemite from the Transvaal, containing 19·45 % TiO_2. If the homogeneous titanomaghemites are accepted as solid solutions between γ-Fe_2O_3 and γ-$FeTiO_3$, which seems the most feasible structure (Nicholls, 1955, p. 143), Basta's measurement allows us to extrapolate to a cube edge of around 8·39 to 8·40 Å. for γ-$FeTiO_3$ provided that Vegard's mixture law is followed in the series.

The very slight increase in the cell-dimension of the spinel phase in E.G. 4359 on heating at 950° C., as contrasted with the appreciable decrease in the cell-dimensions of the accompanying rhombohedral phase, could thus be visualized as due to a one-way migration of Fe^{2+}, Ti^{4+}, and O^{2-} ions from the lamellae into the spinel host, giving rise to a cubic solid solution between Fe_3O_4 and (γ) $FeTiO_3$, at the same time as an exchange of ions ($2Fe^{3+} \rightleftharpoons Fe^{2+} + Ti^{4+}$) between cubic and rhombohedral phases, which would in effect add some Fe_2TiO_4 to the cubic solid solu-

[1] In an abstract of a paper by I. A. Yudin, Some minerals of meteorites, Зап. Всесоюз. Мин. Общ., 1956, vol. 85, p. 403 [Chem. Abstr. vol. 51, no. 5, 3376] mention is made, however, of 'isometric forms of ilmenite . . . observed in the meteoric iron of Sevryukovo'.

tion. This is doubtless a somewhat artificial picture of the process, but will suffice for our purposes.

Fig. 5 shows that each of the heated samples of E.G. 4359 has a sharp Curie point, falling steadily through the series as the Fe_3O_4 becomes diluted with paramagnetic materials, and a completely homogeneous magnetic spinel phase is produced at every stage of the heating experiments. This is consistent with the mechanism of ionic migration and exchange outlined above, and is in striking contrast to the simple homogenization process in the magnetite–ulvöspinel binary series described earlier (p. 635; fig. 2). At the same time the value of the specific saturation magnetization decreases steadily with heating (table IV; fig. 7), and does not reach a constant value early in the process as it does in the magnetite–ulvöspinel binary series.

Fig. 7 shows saturation magnetization plotted against Curie point for the magnetite–ulvöspinel sample C.S.L. 2 (see p. 634), the magnetite–ilmenite sample E.G. 4359, and the magnetite–ulvöspinel–ilmenite sample E.G. 2569 (p. 649), at the various stages of heat-treatment to which they have been subjected. The difference in profile between the curves for C.S.L. 2 and E.G. 4359 is very striking, while that for E.G. 2569 is of the same form as for C.S.L. 2 until the ulvöspinel has redissolved, when it continues in the form of E.G. 4359 as reaction between spinel and rhombohedral phases take place.

This diagram shows clearly the inherent difficulty in correlating Curie point and saturation magnetization in a titaniferous magnetite unless its mineralogical composition and state of exsolution are accurately known, which can seldom be the case.

Each thermomagnetic curve for E.G. 4359 (fig. 5) shows but a single Curie point; the ferri-ilmenite lamellae produced on heating are thus not of the ferromagnetic type (Chevallier *et al.*, 1955; Nicholls, 1955, pp. 139–141). Hence we may as a first approximation use the Curie point to deduce the proportion (f) of Fe_3O_4 in the magnetic spinel phase at each stage of the heating experiments (Chevallier *et al.*, 1955, p. 364). This proportion of Fe_3O_4 may then be referred to the graph prepared by Chevallier *et al.* (1955, p. 361) connecting Fe_3O_4 content with specific saturation magnetization for homogeneous magnetic spinels. Comparison of this saturation (σ_∞) for the spinel phase with the saturation measured on the total heterogeneous intergrowth (σ'_∞) gives the approximate weight percentage ($100\ \sigma'_\infty/\sigma_\infty$) of magnetic spinel. Knowing now the approximate percentage of magnetic spinel in the heated samples and the Fe_3O_4 content of that spinel it is easy to calculate correspondingly the amount of

Fe_2O_3 that must have entered the rhombohedral phase at each stage of the heating, and by difference (knowing that the overall bulk chemical

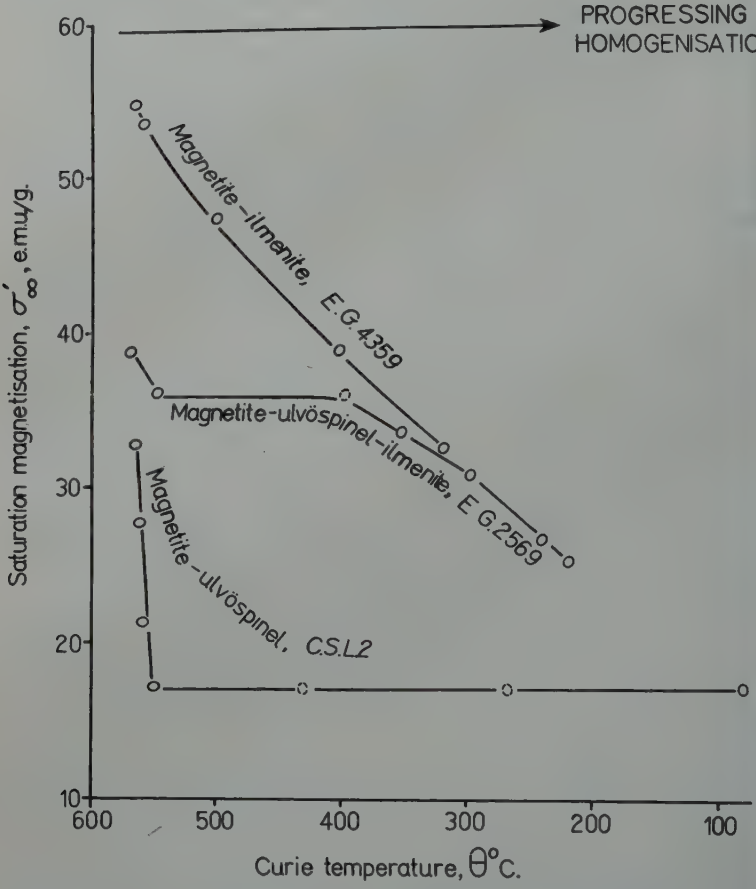


FIG. 7. Saturation magnetization (σ'_∞) for unheated and heat-treated samples plotted against Curie point (θ). Note the characteristic differences in profile for the various types of exsolution assemblage. Broken rings indicate that the sample showed no sharp Curie point.

composition of the samples remains unchanged) the composition of the accompanying spinel phase (table IV). In making such calculations the assumption is made that all the ferric ions made available by the reduction in the quantity of Fe_3O_4 in the spinel phase at each stage of heating enter the ilmenite lamellae to yield an $FeTiO_3$–Fe_2O_3 solid solution; this

is borne out by microscopic and X-ray results. It is further assumed, as a simplification, that the ilmenite lamellae in the original unheated sample contained no Fe_2O_3 in solid solution.

Since the specific saturation magnetization is determined on a weighed sample of heterogeneous intergrowth, calculations of this kind are made on a weight percentage basis. The results for the heated samples of

TABLE IV. Magnetite–ilmenite intergrowth, E.G. 4359: magnetic constants of heated samples, and approximate compositions of phases deduced therefrom (weight %). σ'_∞ and σ_∞ are given for 20° C., in electromagnetic units per g. The total magnetic phase is taken as 100 $\sigma'_\infty/\sigma_\infty$. The numbers in column 1 refer to fig. 8.

			Measured magnetic constants of sample.		Deduced from magnetic constants.		Magnetic spinel phase.				Rhombohedral phase (non-magnetic).		
	Heated.						Total.	MFe_2O_4.	M_2TiO_4.	$MTiO_3$.	Total.	$MTiO_3$.	Fe_2O_3.
No.	° C.	hrs.	θ° C.	σ'_∞.	f(%).	σ_∞.							
1	unheated		565	54·8	95·5	89	61·2	58·5	2·5	(0·2)	32·7	32·7	—
2	500	12	557	53·5	94·0	88	60·8	57·1	3·7	—	33·1	32·2	0·9
3	600	12	495	47·5	84·0	74·5	63·7	53·5	7·4	2·8	30·2	26·8	3·4
4	750	12	400	38·8	71·5	56·5	68·7	49·1	11·5	8·1	25·2	18·7	6·5
5	950	96	316	32·8	63·0	44	74·5	47·0	13·7	13·8	19·4	11·5	7·9
	950	360	317	35·0	—	—	—	—	—	—	—	—	—

Note: In order to achieve closer agreement between normative magnetite, &c., and percentage magnetic phase in the unheated material as deduced from magnetic constants, 0·3 % normative other spinels have been added to normative ferrites to give ferrites 58·5 %; ulvöspinel, &c., 2·5 %; ilmenite, &c., 32·9 %; other spinels 6·1 % (cf. table II).

The 6·1 % of other spinels have been ignored in the above table, so that magnetic spinel and non-magnetic rhombohedral phases total 93·9 % in each case.

E.G. 4359, recalculated to molecular percentages, are presented graphically in fig. 8.

The deduced composition 60 % $FeTiO_3$, 40 % Fe_2O_3, for the rhombohedral phase after heating at 950° C. is compatible with the observed decrease in cell-dimensions (fig. 6) as compared with the unheated intergrowth. From its composition the associated spinel (57 % Fe_3O_4, 26 % $FeTiO_3$, 17 % Fe_2TiO_4) might be expected to have a cubic cell edge of about 8·41 Å., the value actually found by measurement, provided the increase above that of magnetite were due to the 17 % of Fe_2TiO_4 taken into solid solution and there were no appreciable change in cell-dimensions in a pure binary solid solution series between Fe_3O_4 and γ-$FeTiO_3$, as suggested above.

Optical, magnetic, and X-ray observations, then, all indicate compositional changes rather as shown in fig. 8 in the two coexisting phases

when an almost pure magnetite–ilmenite intergrowth is heated at tempera-tures up to 950° C.; it will be noted in table IV that magnetic properties show little appreciable change in samples heated for 4 days and for 15 days at that temperature. In all experiments we have carried out above 950° C. some decomposition of the phases into pseudobrookite and magnetic

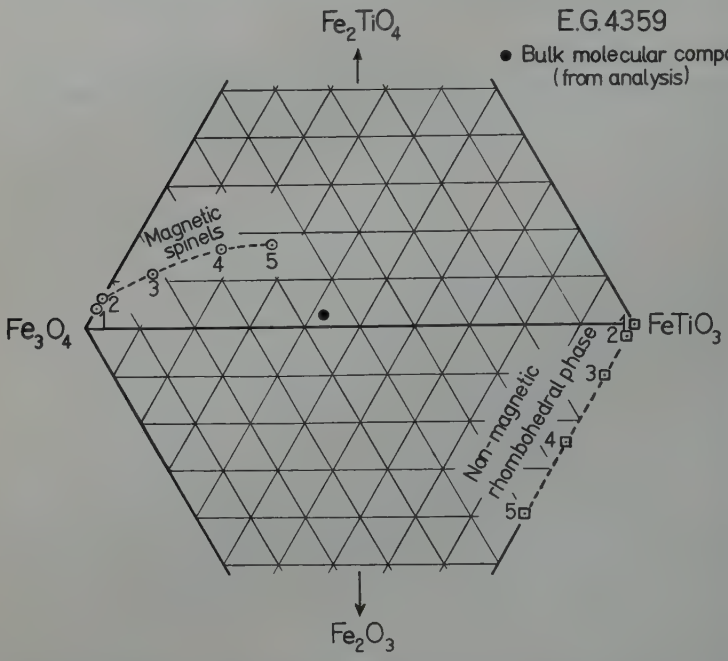


FIG. 8. Approximate compositional changes (mol. %) in coexisting phases of heated magnetite–ilmenite intergrowth E.G. 4359, deduced from magnetic properties. (Numbers refer to stages of heating in table IV.)

spinels has occurred, so that the experiments at 950° C. have probably yielded very nearly the last stage possible in reaction and rehomogeniza-tion of the two phases that can be reached without such decomposition.

Our results appear to confirm the general form of the solvus surface in the Fe_3O_4–Fe_2TiO_4–$FeTiO_3$–Fe_2O_3 part of the system proposed by Nicholls (1955, fig. 13), but do not justify our proposing modifications in detail, while the compositional changes observed on heating agree more or less with this author's predictions of the course of unmixing in an Fe_3O_4–$FeTiO_3$ solid solution. We may visualize a homogeneous spinel on or near the Fe_3O_4–$FeTiO_3$ join unmixing, first probably into two spinels, the one in or

very close to the Fe_2O_3–$FeTiO_3$ binary series rapidly undergoing a monotropic inversion to a rhombohedral ferri-ilmenite. Ionic migration on further cooling would cause the rhombohedral phase to continue changing in composition towards $FeTiO_3$ and the spinel phase towards Fe_3O_4.

Magnetite–ulvöspinel–ilmenite intergrowths.

One example of an intergrowth of all three phases, from a ferrogabbro (E.G. 2569) of the Skaergaard intrusion, has been studied in some detail. Its analysis and norm are given in column 4 in tables I and II, and it will be seen that in bulk composition it falls midway between the two principal binary series.

In reflected light this magnetite is seen to carry very well-defined ilmenite lamellae parallel to {111} and at high magnification the spaces between these lamellae are seen to contain fine thread-like lamellae of ulvöspinel and ilmenite—the latter possibly having originated by oxidation of some of the pre-existing ulvöspinel rather than representing a second generation of direct exsolution bodies (fig. 9).

On heating, we may say that broadly the material first behaves as a magnetite–ulvöspinel intergrowth and then, when all the original ulvöspinel has been taken back into solid solution, reaction takes place in the manner of the magnetite–ilmenite intergrowth E.G. 4359. This can be well seen from the form of the thermomagnetic curves in fig. 9, which in the earlier stages of the heating experiments show the sloping traces characteristic of the re-solution of magnetite and ulvöspinel, and later show the sharp but steadily falling Curie points of the magnetite–ilmenite reaction and re-solution.

The measured magnetic constants of the heated series of samples of E.G. 2569 are given in table V. The approximate compositions of the coexisting spinel and rhombohedral phases may be calculated from the norm and the magnetic constants in the same general manner as outlined above (pp. 643–4) for E.G. 4359: the results, recalculated to molecular percentages, are shown graphically in fig. 10.

Measured lattice parameters for the magnetite and ilmenite phases before and after heating are given below (reflections from the ulvöspinel phase were too broad to permit any reasonable estimation of its cell edge):

	Magnetic spinel.	Ilmenite.		
	a, Å.	*a*, Å.	*c*, Å.	*c*/*a*.
E.G. 2569, unheated ...	8·403±0·001	5·087±0·001	14·09±0·01	2·770
Heated 12 hours at 650° C. ...	8·420±0·002	5·087±0·001	14·09±0·01	2·770
Heated 96 hours at 950° C. ...	8·431±0·001	5·082±0·001	14·04±0·01	2·760

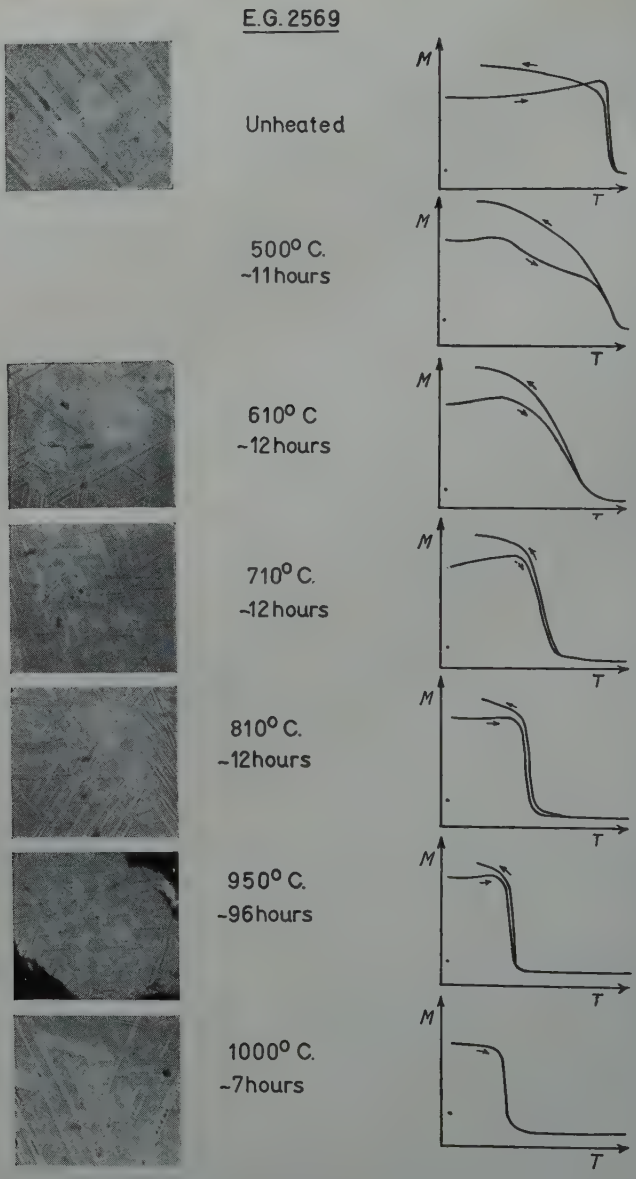


FIG. 9. Photomicrographs (×420, reflected light) and tracings of thermomagneti curves of heated magnetite–ulvöspinel–ilmenite intergrowth E.G. 2569.

TABLE V. Magnetic properties of magnetite–ulvöspinel–ilmenite intergrowth, E.G. 2569, before and after heat-treatment. σ'_∞ is given for 20° C., in electromagnetic units per gram. The numbers in column 1 refer to fig. 10.

No.	Heated. ° C.	hrs.	θ° C.	σ'_∞
1	unheated		567	38·8
2	500	11	547	36·1
3	610	12	*	36·1
—	650	12	*	34·3
4	710	12	349	33·4
5	810	13	292	30·7
6	950	96	236	26·8
—	950	96	240–50	27·7
7	1000	7	220	25·5

* Indicates that the heated sample did not show a sharp Curie point.

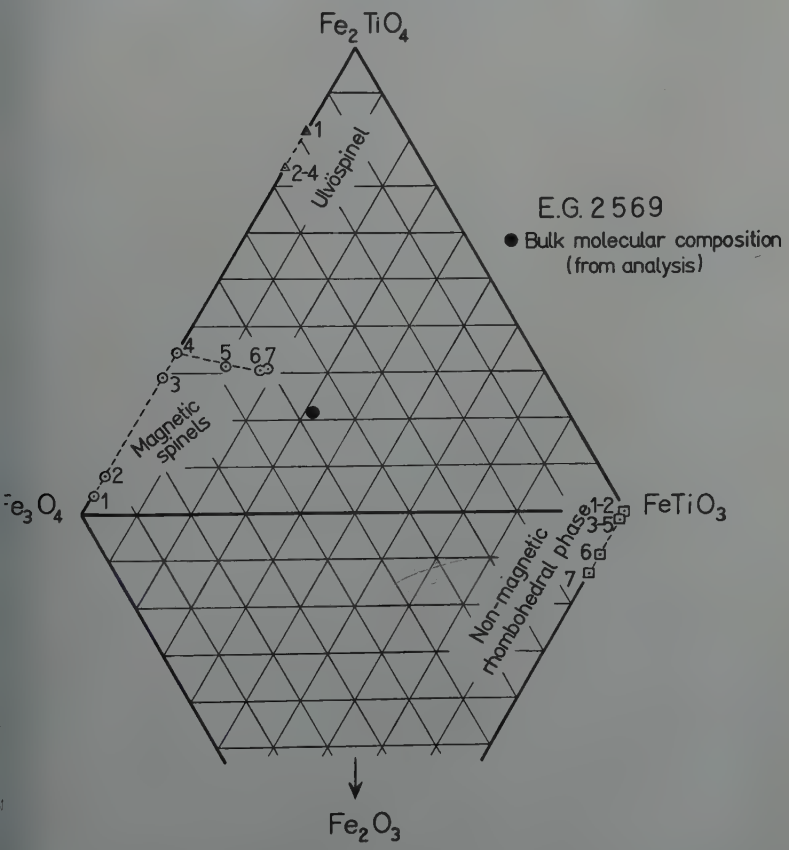


FIG. 10. Approximate compositional changes (mol. %) in coexisting phases of heated magnetite–ulvöspinel–ilmenite intergrowth E.G. 2569, deduced from magnetic properties. (Numbers refer to stages of heating in table V.)

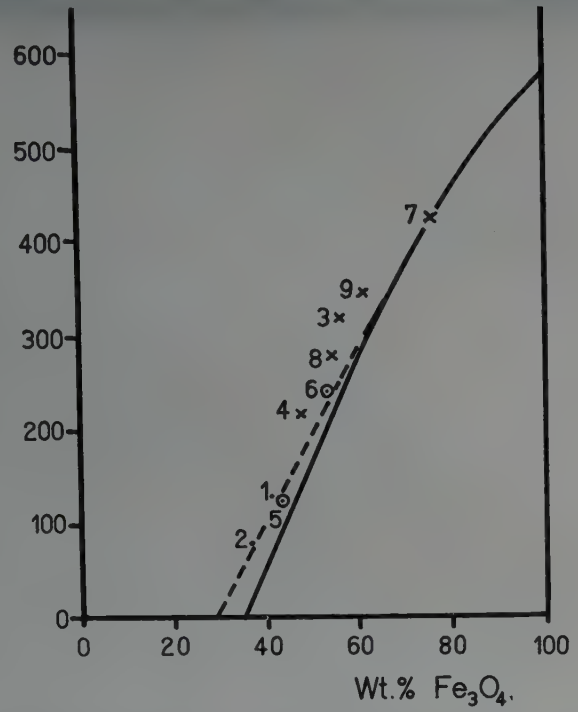
As in the case of the pure magnetite–ilmenite intergrowth E.G. 4359 the changes in lattice parameters on heating agree quite well with th changes in composition of the phases deduced magnetically. The valu $a = 8{\cdot}431$ Å. for the spinel phase after heating at 950° C. is appropriat for the content of around 30–35 mol. % Fe_2TiO_4, assuming once agai that the (γ) $FeTiO_3$ component of the final solid solution has little or n effect upon the cell-dimensions.

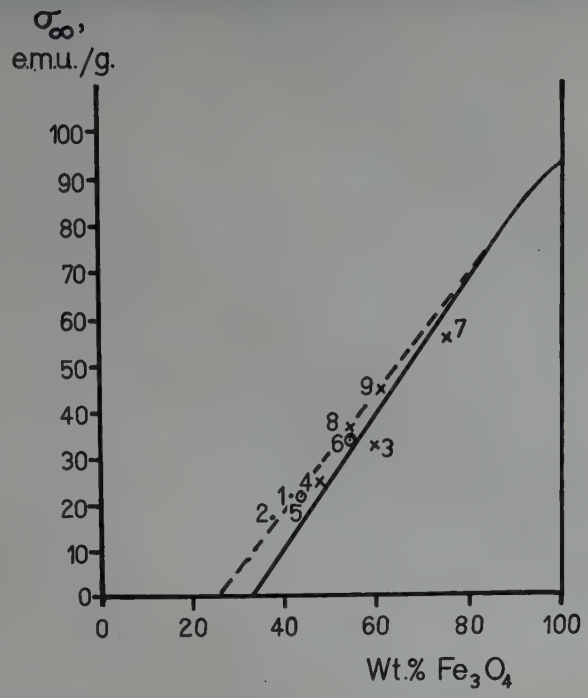
The cell-dimensions of the rhombohedral phase of E.G. 2569 hav changed much less on heating than the corresponding phase in the pur magnetite–ilmenite intergrowth E.G. 4359, the final parameters indicat ing an ilmenite with perhaps about 10 % Fe_2O_3 in solid solution. Thi again is in fair agreement with the magnetic deductions (fig. 10) and wit microscopic observation, since the rhombohedral lamellae in this heate sample retain a darker tint and far more marked reflection pleochroism than the ferri-ilmenite lamellae developed in E.G. 4359 when heated t the same temperature.

Materials not studied in detail.

As well as the four intergrowths already described in detail, heatin experiments and some magnetic measurements have been carried out o five other titaniferous magnetites (Analyses nos. 5–9 in tables I and I and fig. 1). The results are set out in table VI. The original materia are all intergrowths of all three phases: magnetite, ulvöspinel, and ilmen ite, in varying proportions, and in no case has absolute homogeneit (as observable microscopically) been attained by heating at 950° C although two samples (C.S.L. 3 and E.G. 4355, lying near the Fe_3O_4 Fe_2TiO_4 join) closely approach homogeneity.

Figs. 11 and 12 show curves constructed by one of us (R.C.) relatin Curie point and specific saturation magnetization respectively with weigh percentage (f) of Fe_3O_4 in homogeneous natural titanomagnetites. Thes curves are slightly revised from those already published (Chevallier *et al.* 1955), being improved at the magnetite-rich end by the inclusion o magnetic data recently obtained on titanium-poor magnetite–ulvöspin solid solutions separated from East African carbonatites and chemicall analysed (E.A.V.). In the region of low Curie points, however, the curve are based only upon samples from Ankaratra (Madagascar), which contai between 8 and 10 % Al_2O_3 and 3·7 to 6·7 % MgO (Chevallier *et al.*, 195 pp. 338–9). Naturally occurring, structurally homogeneous titanomagn tites with such low Curie points are somewhat rare, and the curves a perhaps less well defined in this region than in the regions closer to Fe_3O





FIGS. 11 (*left*) and 12 (*right*). Curves relating weight percentage (f) of Fe_3O_4 in homogeneous titanomagnetites with Curie point (θ) and saturation magnetization (σ_∞) respectively. θ and σ'_∞ for samples heated at 950° C. inserted: • completely homogenized; ⊙ homogenization almost complete; × homogenization incomplete. (Numbers refer to analyses in table I.)

The observed values of θ and σ'_∞ for our nine samples heated to 950° C have been inserted in figs. 11 and 12, using as the value for the abscissa in each case the limiting weight percentage of Fe_3O_4 (table II), i.e. the Fe_3O_4 percentage corresponding to the total Fe_2O_3 revealed by analysis since in completely homogeneous titanomagnetites all the Fe''' ions may be regarded as contributing towards the formation of Fe_3O_4.

TABLE VI. Magnetic properties of various titanomagnetites before and after heating. σ'_∞ is given for 20° C., in electromagnetic units per gram.

Anal.		Normative mol. %.			Heated.		Measured magnetic constants.	
		Fe_3O_4	Fe_2TiO_4	$FeTiO_3$				
no.	Sample.	&c.	&c.	&c.	° C.	hrs.	θ° C.	σ'_∞
5	C.S.L. 3	44·0	41·7	14·3	unheated		563	53·1
					450	12	558	29·6
					500	12	556	25·4
					950	16	120	22·1
6	E.G. 4355	55·7	33·4	10·9	unheated		565	48·6
					450	12	557	41·5
					500	12	556	38·7
					550	12	551	36·4
					650	12	*	36·6
					950	16	247	33·6
7	C.S.L. 5	75·2	8·4	16·4	unheated		563	68·3
					950	16	429	55·6
8	E.G. 4353	58·3	25·2	16·5	unheated		552	50·6
					450	336	550	43·3
					950	96	286	36·4
9	E.G. 4430	60·2	10·5	29·3	unheated		564	56·6
					950	18	350	44·5

* Indicates that the heated sample did not show a sharp Curie point.

After heating at 950° C. C.S.L. 3 and E.G. 4355 appear at least 95 % homogeneous under the microscope, a very few rods and small granules of ferri-ilmenite remaining; C.S.L. 5 and E.G. 4353 appear about 90 % homogeneous, E.G. 4430 80 % homogeneous, lamellae of ferri-ilmenite remaining.

The samples that have been completely homogenized (analyses nos. 1 and 2) or very nearly homogenized (5 and 6) by heating tend to define a (broken) line deviating from the original curve (fig. 11) at Curie points below about 300° C. This modified curve may prove to be more accurate than the original, although the latter has been used in this paper for calculating the approximate compositions of the coexisting phases in the heated magnetite–ilmenite intergrowths described in earlier sections. It is likely that titanomagnetites homogenized by heating to a high temperature and suddenly quenched, as in our experiments, will have

somewhat disordered structures with regard to the distribution of Fe″, Fe‴, and Ti^{IV} between the available lattice sites. It has been found by Gorter (1954) and commented upon by Nicholls (1955, p. 134) that such disorder in certain ferrites may lead to some increase in both Curie point and saturation magnetization over the values to be anticipated were the substances in stable structural equilibrium (e.g. in the case of Fe_3O_4–Fe_2TiO_4 solid solutions, having the true inverse spinel structure).

We do not assert at present, therefore, that the broken curves in figs. 11 and 12 should be substituted for the original ones, even though the latter are based upon magnetites with rather high contents of Al and Mg. The true relationships between Fe_3O_4 content and magnetic constants may well be represented by curves lying somewhere in between the two cases.

Conclusions.

At high temperatures fairly extensive solid solution probably exists over much of the magnetite–ulvöspinel–ilmenite compositional field, and homogeneous titanomagnetites of widely varying composition and magnetic properties may persist without unmixing in some rapidly cooled lavas. The composition of the titanomagnetite is sensitive to changes in oxidation-reduction relationships between crystals and magma, and a magnetite that remains strongly reduced during cooling (i.e. in or near the Fe_3O_4–Fe_2TiO_4 binary spinel series) may be expected to remain homogeneous down to much lower temperatures than one in the Fe_3O_4–$FeTiO_3$ binary series. Once it unmixes, however, the magnetic phase will always be rather close to Fe_3O_4 (see fig. 4), which can be expected to cause a rather sudden rise in the Curie point of the mineral as exsolution commences. The lack of a sharp Curie point observed in some lavas may be due to varying degrees of exsolution in different grains of titaniferous magnetites in or near the Fe_3O_4–Fe_2TiO_4 series.

A titanomagnetite solid solution crystallizing with an original composition in or near the Fe_3O_4–$FeTiO_3$ binary series, or which changes its composition towards this series by oxidation, may be expected to exsolve an $FeTiO_3$–Fe_2O_3 solid solution which may at first be a spinel, but which rapidly inverts to a rhombohedral ferri-ilmenite. The initial exsolution will take place at a much higher temperature than in the Fe_3O_4–Fe_2TiO_4 series, but we have no data to suggest a possible temperature. On further cooling both rhombohedral and spinel phases change in composition until they closely approach $FeTiO_3$ and Fe_3O_4 respectively. Experience of the ore minerals commonly occurring in igneous rocks suggests that the

exsolution and this compositional change take place rather rapidly since few rocks have been described in which ferri-ilmenite lamellae have been identified in the magnetite. It is of interest, however, that Nagata (1953) and Uyeda (1955) describe an intergrowth of magnetite ferri-ilmenite and inverse magnetic spinel in the celebrated reversely magnetized Haruna (Japan) dacite pumice. This type of intergrowth may well have originated by exsolution and incomplete ionic migration in a member of the Fe_3O_4–$FeTiO_3$ series. The ferri-ilmenites produced in our heating experiments are not ferromagnetic, but this could well be due to structural disorder in the rapidly quenched samples.

The reaction relationship observed between spinel and rhombohedral phases in our heating experiments leads to the spinel phase always showing a sharp Curie point—in contrast to intermediate heated samples in the magnetite–ulvöspinel series; partly unmixed non-equilibrium minerals in the magnetite–ilmenite series may thus equally be expected to show sharp Curie points and successively greater saturation magnetization as final equilibrium is approached.

Microscopic study and magnetic behaviour of a sample containing exsolved ulvöspinel as well as ilmenite suggest that exsolution and organization of broad ilmenite lamellae parallel to {111} was complete before exsolution of ulvöspinel occurred, and that a second period of ilmenite exsolution or partial oxidation of the exsolved ulvöspinel at still lower temperatures may lead to a second generation of less well organized ilmenite lamellae.

In conclusion it must be emphasized that the variations observed in thermomagnetic curve, Curie point, and saturation magnetization with degree of homogenization in our experiments (and hence of exsolution) depend very much on whether the mineral is a member of the Fe_3O_4–Fe_2TiO_4 series, or the Fe_3O_4–$FeTiO_3$ series, or is intermediate between the two. This is of great importance to the geophysicist concerned with rock magnetism, and adequate correlation between magnetic constants, lattice parameters, and chemical composition will only be attained in those cases where the magnetic minerals have been separated from the rocks in a very high state of purity, examined carefully with the microscope, and the chemical analysis carried out accurately and in detail (not merely confined to FeO, Fe_2O_3, and TiO_2), so that the position of the mineral relative to the two main binary series can be established. The assumption that is sometimes made that the apparently homogeneous titaniferous magnetites of lavas are always essentially Fe_3O_4–Fe_2TiO_4 solid solutions cannot be supported.

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Plagioclases from the Juvinas meteorite and from allivalite from the Isle of Rhum.

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[Read 7 November 1957.]

Summary. The optical properties and specific gravity, and the variations in thes properties, of analysed plagioclases separated from the meteorite (eucrite) fro Juvinas, France, are compared with the corresponding values for a terrestri plagioclase of almost identical composition from an allivalite from Rhum. The rang in properties for the Juvinas plagioclase indicates a compositional range from abo $Ab_{35}An_{65}$ to $Ab_{15}An_{85}$, but the great majority of grains are bytownite with approx mately 83 % (molecular) anorthite.

The frequency of occurrence of the twin-laws of the Juvinas plagioclase resembl that of plagioclase from basalts and allied rocks.

The variable changes and, in some grains, absence of change in the optic properties shown by the Juvinas plagioclase crystals, after heating to 1100° C. f 48 hours followed by rapid cooling, contrasts with the small but constant optic changes shown by the allivalite plagioclase (for which geological evidence indicat slow cooling) after identical heat treatment. It is inferred that the meteoritic plagi clase grains have had differing thermal histories, and that some grains have be subjected to previous natural quenching.

THE main object of this investigation was to collect precise optic data (including optical changes on heating) for the calcic plagi clases of the eucritic meteorites, and to compare the results with tho obtained from terrestrial plagioclases.

It was hoped that such information might give further clues to t geological history of this type of meteorite. It was also hoped that t optical data might complement the recent X-ray data of Gay and othe as a guide to structural changes produced by heating plagioclases of th composition. Of the stony meteorites, the eucrites and howardite though few in numbers, offer the most promising field for a study meteoritic plagioclases. The eucrite from Juvinas, France (B.M. 9026 was chosen for this investigation because of the relative abundance material and because some X-ray work has already been done upon i felspar. Much briefer examinations were made of the plagioclases fr the Pasamonte and Vaca Muerta stones.

The intended comparison of meteoritic felspars with their earth counterparts required the use of a terrestrial plagioclase as a 'contr

upon the investigation. For this purpose the bytownite from the banded allivalite of Barkeval Pass, Rhum (B.M. 1923, 476 [21]), was chosen because of its suitable composition, freshness, and ease of separation.

Determinations were made of the refractive index, the optic axial angle, and the orientation of the indicatrix; the last two properties were also remeasured after heat treatment. Studies were also made of the twin-laws, the specific gravity, and the chemical composition.

Methods.

Separation. The first separation of felspar from Juvinas was done by S. W. F. Patching and L. D. Muller of the Atomic Energy Research Establishment at Harwell using an induced roll magnetic separator followed by a Frantz magnetic separator. Subsequent separations (of additional material) and all separations of plagioclase from the allivalite were made in the Department of Mineralogy, British Museum (Natural History), using the Cook magnetic separator. After suitable sizing, the material was repeatedly fed into the separator, the current being progressively increased and the non-magnetic fraction being collected on each occasion until quite free of foreign material. This gave pure samples, uncontaminated by heavy liquids, which were used for the chemical analysis, and for the determinations of specific gravity and refractive index.

Refractive indices. The β index was determined by the immersion method, using mixtures of eugenol and cinnamic aldehyde. The index of grains showing the central emergence of an optic axis was matched against that of the liquid in sodium light. The refractive index of the liquid was then determined on a Bellingham and Stanley refractometer, which had previously been calibrated against two test pieces of glass having indices close to that of the plagioclase.

Optic axial angle. 2V was measured on a Leitz 4-axis universal stage, which had previously been checked with a test piece of topaz of known optic axial angle.[1] Each optic axis was measured ten times in the 45° orientation and ten times in the 135° orientation. The data for 2V are based upon crystals in which both optic axes were directly observable.

The orientation and 'twin-angle' values were also determined on the calibrated universal stage. The crystallographic directions were obtained as the twin axes of the various twin-laws and not from cleavages or crystal boundaries, since these latter have been shown by previous investigators to give greater scatter of poles than do the twin-axes.[2] In

[1] Kindly sent by H. W. Fairbairn of the Massachusetts Institute of Technology.

[2] See, for example, H. Tertsch, Tschermaks Min. Petr. Mitt. 1941, vol. 53, p. 56.

general eight to ten measurements were made of each optic vector. It was found that grains so oriented that the three indicatrix axes were about equally inclined to the section normal usually gave less accurate right-angled triangles than grains having one axis near the normal. The accuracy of the stereographic net was checked before beginning the measurements, and the same net was used throughout.

The twin-laws (Juvinas plagioclase only) were obtained directly from the twin-angle values, which have now been published for the majority of twin-laws and plagioclase compositions. A rapid plot, constructed from a single measurement of each observable optic vector, usually sufficed to establish the twin-law. The few remaining ambiguous instances were resolved by locating the twin-axis and transposing in the usual way. In order to ensure a random sample, traverses were made across the section at equal intervals and grains equally spaced in each traverse were chosen for determination of the twin-law.

The specific gravities were determined in a diffusion column, which was prepared by the careful addition of a bromoform-benzene mixture to a lower bromoform layer in a graduated cylinder; from about 24 to 48 hours after the liquid addition an approximately linear relationship existed between height in the column and specific gravity. The column was calibrated by the insertion of mineral grains the specific gravities of which were determined by suspension in heavy liquid mixtures.

Heating technique. The method used was that described by H. G. Owen,[1] the section being mounted on a slide of vitreous silica, and heated in a tube furnace with a platinum–platinum-rhodium thermocouple to a temperature of 1100° C. for a period of 48 hours. Rapid quenches were not attempted owing to risk of fracture. By this means it proved possible to remeasure after heating the same crystals as had been measured before heating, and to detect small optical changes with greater certainty than is possible from determinations on different grains.

Chemical analysis. The four major constituents were each determined by at least two independent methods to eliminate, as far as possible, systematic errors. A direct colorimetric comparison was made of the SiO_2 percentages of the two felspars in order to confirm the virtual identity of their composition.

Results.

Refractive index. The histogram (fig. 1) shows the results of thirty-three determinations of β on the plagioclase of the allivalite and the sam

[1] Min. Mag. 1957, vol. 31, p. 426.

number on the Juvinas plagioclase. The allivalite felspar measurements form a symmetrical distribution; the mean value of β is 1·5760 with a standard deviation[1] of $\pm$0·0010 (equivalent to a range of 1·9 % in anorthite).

By contrast the Juvinas plagioclase measurements form a slightly

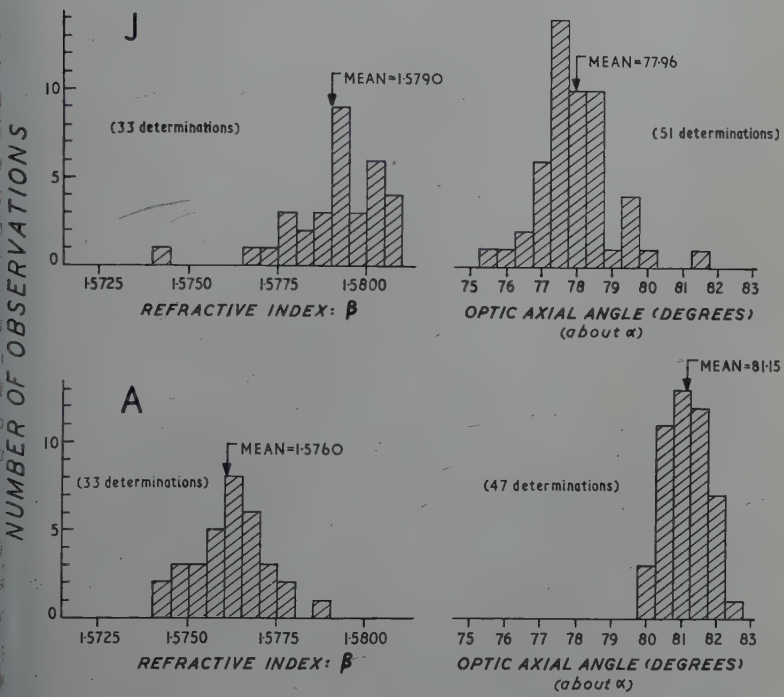


FIG. 1. Refractive index and optic axial angle ranges: A = allivalite; J = Juvinas. The difference between the refractive index mean values corresponds to a $5\frac{3}{4}$ % anorthite difference. The difference between the optic axial angle mean values corresponds to a $6\frac{3}{4}$ % anorthite difference.

skew' distribution with one abnormally low value. Proof of the validity of this low result and corroboration of the asymmetry of the distribution is given by the subsequent discovery, during the diffusion column experiments, of grains with an even lower refractive index (lowest value of $\beta = 1{\cdot}5710$). The refractive index distribution for Juvinas consists, essentially, of a 'main group' with limits of 1·577 to 1·581 and a 'tail' extending from 1·577 to 1·571. The overall mean is 1·5790$\pm$0·0013.

[1] In this and all subsequent standard deviations, the small sample correction has been applied.

Optic axial angle. The histogram (fig. 1) shows the results of forty-seven determinations of 2V on the allivalite and fifty-one on the Juvinas felspars. The distribution for the allivalite plagioclase is symmetrical; the mean value of 2V about α is $81{\cdot}1° \pm 0{\cdot}60°$ (equivalent to a range of 0·9 % in anorthite).

The distribution for the Juvinas plagioclase is approximately symmetrical at its centre. There is, however, a much greater lateral spread than for the allivalite felspar and there is a suggestion in the histogram of a small subsidiary peak towards the higher angular values. The mean value of 2V is $78{\cdot}0° \pm 1{\cdot}03°$.

Orientation of indicatrix. The crystal directions $\perp$ (010), [001], and $\perp$ [001] in (010) were determined in relation to a fixed indicatrix with β at its centre and are shown, superimposed on W. Nikitin's migration curves,[1] in fig. 2. The mean positions of the three poles for the allivalite plagioclase lie on or very close to the curves at points representing 87 to 89 % anorthite. The alignment of the three directions with M. Reinhard's curves[2] is poorer. The (010) pole, for example, lies 3 mm. to the right of its curve.[3] For the Juvinas plagioclase the mean positions indicate a composition of 91 to 93 % anorthite; with the exception of the [001] pole, which falls about 2 mm. to the right (on the 20 cm. scale), the points again lie very close to the Nikitin curves. The scatter of points representing the (010) and [001] directions is considerably greater for the Juvinas than for the allivalite plagioclase. The scatter for $\perp$ [001] in (010) is similar for both felspars.

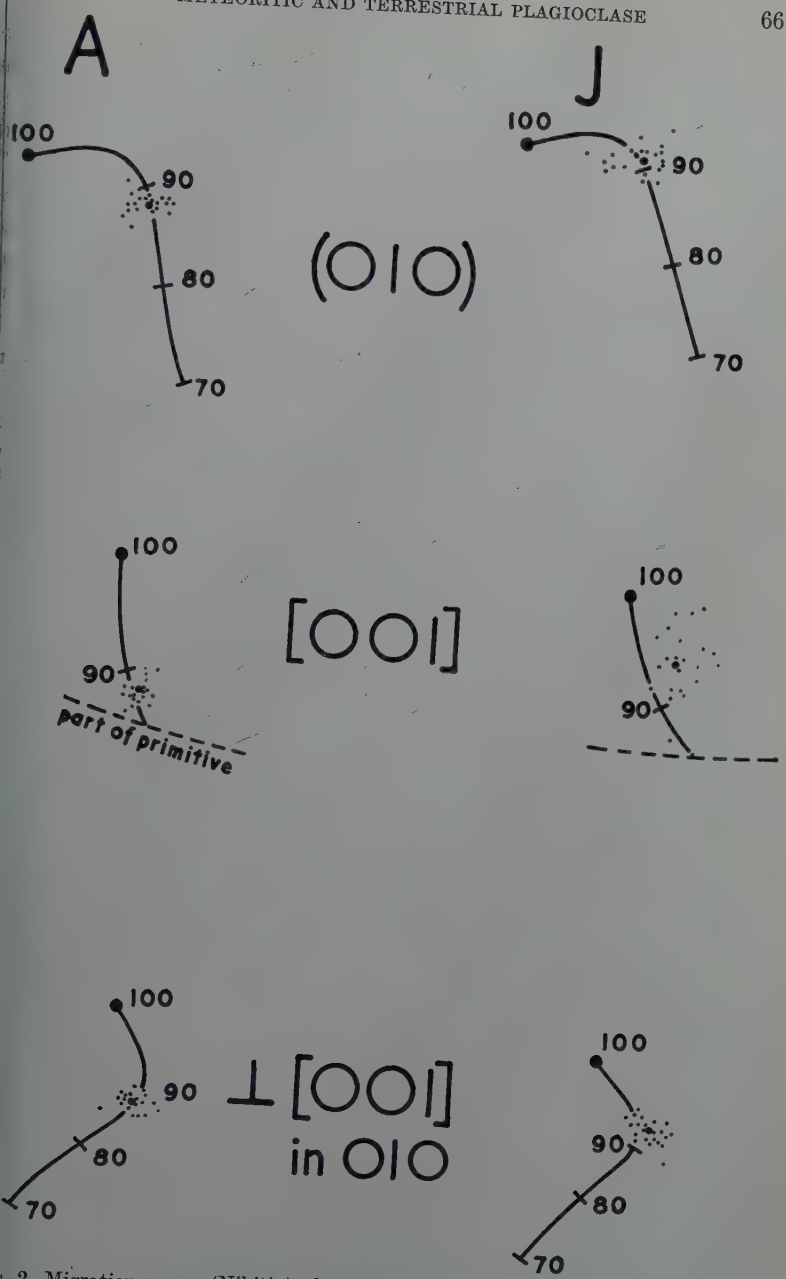
A more sensitive test of orientation than the plotting of crystal directions is afforded by the values of the 'twin-angles'. These are the angles between each axis of the indicatrix of one twin-member and the corresponding axis of the indicatrix of the other member, viz. the angles $\alpha\alpha_1$, $\beta\beta_1$, and $\gamma\gamma_1$, where $\alpha\,\beta\,\gamma$ are the indicatrix axes for one member and $\alpha_1\,\beta_1\,\gamma_1$ for the other of the twin-pair. The change in these angles with changing orientation is twice the change in the angles between α, β, or γ and the twin-axis. Moreover the twin-angles are obtained directly from the stereogram without transposal or location of the twin-axis; they are therefore not subject to the possible small plotting errors arising from these operations.

Additional twin-angle values can be obtained if the optic axes have been located for each twin-member. Thus if A and B be the two optic

[1] Die Fedorow-Methode. Berlin, 1936, fig. vi.

[2] Universaldrehtischmethoden. Basel, 1931.

[3] These curves are drawn on a stereographic projection of radius 10 cm.



4. 2. Migration curves (Nikitin) of the poles of (010), [001], and ⊥ [001] in (010), wing the plotted positions of the poles for the allivalite and Juvinas plagioclases: A = allivalite; J = Juvinas.

axes for one member and A_1 and B_1 be the optic axes for the other, four angles can be measured, namely AA_1, BB_1, AB_1, and BA_1. It was found, however, that of these four angles only BB_1 is of practical use in the present investigation. Therefore the twin-angles to which reference is made are $\alpha\alpha_1$, $\beta\beta_1$, $\gamma\gamma_1$, and BB_1, measured over the twin-axis.

The values of these angles, and the standard deviations (expressing

TABLE I. Twin-angle values $\alpha\alpha_1$, $\beta\beta_1$, $\gamma\gamma_1$, and BB_1 (see text) for allivalite and Juvinas plagioclases. Each figure is the mean of determinations on ten crystals and the standard deviation* $\hat{\sigma}$ for each group is cited. The percentages of anorthite given are deduced from the values of $\alpha\alpha_1$, $\beta\beta_1$, and BB_1, for albite twins only (see text)

Twin-law.	Albite.		Carlsbad.		Albite-Carlsbad.		% Anorthite (albite law only).	
	Angle.	$\hat{\sigma}$.	Angle.	$\hat{\sigma}$.	Angle.	$\hat{\sigma}$.		
Allivalite $\alpha\alpha_1$	63½	1·0	107½	1·4	31	0·8	85	mean 87
$\beta\beta_1$	58	1·4	177	1·6	57½	1·4	—	
$\gamma\gamma_1$	91¼	1·1	72¼	1·4	47	0·8	90	
BB_1	6¾	0·9	9	1·0	6½	0·5	86½	
Juvinas $\alpha\alpha_1$	66¾	1·6	106½	1·2	28½	1·6	90	mean 93
$\beta\beta_1$	57	2·4	172½	2·5	58½	1·7	—	
$\gamma\gamma_1$	93⅔	1·9	73	1·2	49¾	1·4	98	
BB_1	1¼	0·7	9¾	2·5	9	1·2	92	

* The small sample correction $\sqrt{n}/(n-1)$ has been applied.

the scatter of these values) are given in table I for albite, Carlsbad, and albite-Carlsbad twins of the allivalite and Juvinas plagioclases. It is seen that, for most angles, the standard deviations are considerably greater for the Juvinas than for the allivalite felspars. Derivation of the plagioclase composition from these angular values can only be approximate on account of the uncertainty, at this composition, of the published curves. However, the curves for $\alpha\alpha_1$, $\gamma\gamma_1$, and BB_1 for albite twins have a sufficiently steep and uniform slope to make it possible at least to estimate the compositional difference between the two felspars, and the result[1] (table I) indicates a 6 % higher anorthite content for the plagioclase from Juvinas.

Zoning. No zoned plagioclases were seen in the allivalite sections and zoning is not conspicuous in the Juvinas plagioclase, although a few grains show 'patchy' extinction suggestive of some granulation and stress. In those rare Juvinas crystals in which zoning does occur it is

[1] Composition derived from the curves by H. Tertsch, Tschermaks Min. Petr. Mitt., 1942, vol. 54, figs. 4*a* and 6*a*. The An percentages are based on the high temperature curves because of the greater consistency in the values interpolated on these curves rather than on the low temperature curves.

of normal type: a relatively narrow outer zone of more sodic plagioclase, rather sharply separated from the 'core'. No measured difference between outer and inner zones exceeded 5 % anorthite. Compositional differences of this order were found to result in 5 to 6° triangles of error for the twin-axis, as located from the indicatrix for the inner zone of one twin-lamella coupled with the indicatrix for the outer zone of the other lamella. This is of interest because similar triangles of error were obtained for many unzoned Juvinas crystals (though they were never observed in the allivalite felspars). It must therefore be assumed that composition differences of this magnitude (5 % anorthite content) frequently occur between the paired lamellae of the Juvinas twinned crystals. On heating to 1100° C. (see p. 666) these differences are removed and the crystals become homogeneous.

Results of heat treatment. The aim of these experiments was to measure the effect of heat upon the optic axial angle and the orientation. Since the changes were expected to be small it was considered necessary, before heating, to determine the precision with which both 2V and the twin-angle values can be measured. Pairs of measurements were, therefore, made upon sufficient grains to evaluate the probable error of a determination. Fifteen measurements of 2V gave a standard deviation of 0·4°. Fifty-five measurements of twin-angle values gave a standard deviation of just under $1\frac{1}{4}$°.

Differences exceeding twice the value of the standard deviation are usually accounted significant. It may therefore be reckoned that differences in 2V measurements of 0·8° and in twin-angle values of $2\frac{1}{2}$° are significant differences.

Effect of heat on the optic axial angle. Plagioclase from allivalite. Remeasurement of 2V in eighteen crystals after heating at 1100° C. for 48 hours gave the results shown in table II. The smallest increase of angle after heating is well above the significance level. A small increase in 2V is thus established beyond doubt. The consistency of the figures for increase is a feature of the table. More than half the individual results are within $\frac{1}{3}$° of the mean value of increase, viz. $2\frac{3}{4}$°.

Plagioclase from Juvinas. The small proportion of suitable felspars in thin sections of the meteorite and the experimental difficulties limited the size of the sample to fourteen grains, the results for which are also given in table II. The inference from these figures is of both a smaller and a more variable increase in 2V for the meteoritic than for the terrestrial plagioclase. Two Juvinas crystals actually gave a smaller 2V after heating (though neither of these changes is statistically significant). Only two

crystals showed increases comparable with the mean increase shown by the allivalite felspar.

Effect of heat on twin-angle values. Plagioclase from allivalite. The changes on heating in the values of $\alpha\alpha_1$, $\beta\beta_1$, $\gamma\gamma_1$, and BB_1 were measured for seven grains showing albite twins and for six grains twinned on the

TABLE II. Effect of heat treatment (48 hours at 1100° C.) upon the optic axial angle of allivalite and Juvinas plagioclases.

Allivalite.

2V before heating.	2V after heating.	Change in 2V.	2V before heating.	2V after heating.	Change in 2V.
81·45	82·60	+1·15	81·40	84·05	+2·65
81·20	83·60	+2·40	80·80	83·30	+2·50
80·35	84·05	+3·70	81·20	83·70	+2·50
80·35	83·45	+3·10	80·40	82·75	+2·35
80·35	83·70	+3·35	81·10	83·70	+2·60
81·70	84·20	+2·50	80·85	83·30	+2·45
80·50	83·55	+3·05	80·70	82·95	+2·25
81·20	84·50	+3·30	81·10	82·95	+1·85
81·30	84·15	+2·85	81·20	85·70	+4·50
		Means	80·95	83·68	+2·73±0·73

Juvinas.

77·50	79·70	+2·20	76·85	78·15	+1·30
77·65	78·75	+1·10	77·50	79·35	+1·85
78·30	79·50	+1·20	77·60	78·80	+1·20
79·50	82·05	+2·55	78·30	80·45	+2·15
78·40	78·30	−0·10	77·70	79·25	+1·55
78·00	80·05	+2·05	78·05	77·40	−0·65
76·40	78·65	+2·25	78·75	81·80	+3·05
		Means	77·89	79·44	+1·55±1·00

* Standard deviation; the small sample correction has been applied.

Carlsbad law. Only one crystal with an albite-Carlsbad twin could be remeasured after heating; it was not therefore possible to get significant results for albite-Carlsbad crystals. In order to save space only the changes in the angular values (and not the values themselves) are given in table III. The changes in $\beta\beta_1$ for both twin-laws are below the significance level. The changes in $\alpha\alpha_1$ and $\gamma\gamma_1$, though only just statistically significant, undoubtedly reflect an actual shift in the indicatrix, for the individual values have the same sign throughout. The change in BB_1 is quite marked. As a trial showed, one measurement made from a single setting of each B optic axis would have sufficed to measure BB_1 with sufficient accuracy to detect the change after heating.

TABLE III. Effect of heat treatment (48 hours at 1100° C.) upon the twin-angle values (see text) for allivalite and Juvinas plagioclases (value before minus value after heating).

		Allivalite.				Juvinas.			
		$\alpha\alpha_1$.	$\beta\beta_1$.	$\gamma\gamma_1$.	BB_1.	$\alpha\alpha_1$.	$\beta\beta_1$.	$\gamma\gamma_1$.	BB_1.
Albite twins		$-3\frac{1}{2}$	$-2\frac{3}{4}$	$-5\frac{3}{4}$	$+5$	0	$-1\frac{1}{2}$	-2	$+1\frac{1}{4}$
		$-\frac{1}{2}$	$-1\frac{1}{2}$	$-2\frac{1}{2}$	$+3$	$-\frac{1}{4}$	$-\frac{1}{4}$	0	0
		$-\frac{1}{2}$	$-2\frac{1}{2}$	$-1\frac{3}{4}$	$+5$	$-\frac{1}{2}$	$-2\frac{1}{2}$	$-\frac{1}{2}$	—
		$-2\frac{1}{4}$	$-1\frac{1}{2}$	-3	$+3\frac{1}{2}$	$-2\frac{1}{2}$	$+4\frac{1}{2}$	$+2\frac{1}{2}$	—
		$-2\frac{1}{2}$	$+\frac{1}{2}$	$-1\frac{1}{2}$	$+5$	$-4\frac{1}{2}$	$+2\frac{1}{2}$	$-3\frac{1}{4}$	$-\frac{1}{2}$
		-2	$-\frac{1}{2}$	$-1\frac{1}{2}$	$+3\frac{3}{4}$	$-\frac{1}{2}$	$-1\frac{1}{2}$	$-2\frac{1}{2}$	$+3\frac{1}{2}$
		$-3\frac{1}{4}$	$-1\frac{1}{4}$	$-3\frac{1}{2}$	$+5\frac{1}{4}$	$-2\frac{3}{4}$	$+\frac{1}{2}$	$-2\frac{1}{2}$	$+\frac{1}{2}$
						-2	$-\frac{1}{2}$	$-1\frac{1}{2}$	—
						$-2\frac{1}{4}$	$+3\frac{3}{4}$	$+\frac{1}{2}$	$+5$
						$+2\frac{1}{2}$	$-3\frac{1}{2}$	-1	-2
Means		-2	$-1\frac{1}{4}$	$-2\frac{3}{4}$	$+4\frac{1}{2}$	$-1\frac{1}{4}$	0	-1	$+1$
Carlsbad twins		$-2\frac{1}{2}$	0	$+3$	$+4\frac{3}{4}$				
		$-\frac{1}{2}$	$+3\frac{3}{4}$	$+1$	$+4\frac{1}{2}$				
		-3	$+\frac{3}{4}$	$+2\frac{1}{2}$	$+5\frac{1}{4}$	$-3\frac{1}{2}$	$+1$	$+2\frac{1}{2}$	—
		$-2\frac{1}{4}$	0	$+2\frac{1}{4}$	$+4\frac{1}{4}$	-4	0	$+3\frac{1}{2}$	$+\frac{1}{4}$
		$-2\frac{1}{4}$	0	$+2$	$+3\frac{3}{4}$				
		$-2\frac{1}{4}$	0	$+1\frac{1}{2}$	$+4$				
Means		$-2\frac{1}{4}$	$+\frac{3}{4}$	$+2$	$+4\frac{1}{2}$	$-3\frac{3}{4}$	$+\frac{1}{2}$	$+3$	$+\frac{1}{4}$

The interpretation of these angular changes is shown diagrammatically in fig. 3. The diagram combines the angular changes shown by both the albite and the Carlsbad twinned crystals. It shows that there is a rotation of about 2° of the indicatrix about β (i.e. a rotation in the plane of the optic axes). This rotation, combined with an increase in 2V of about $2\frac{3}{4}$°, keeps the position of the A optic axis almost unchanged, while the B optic axis moves about $4\frac{1}{2}$°.

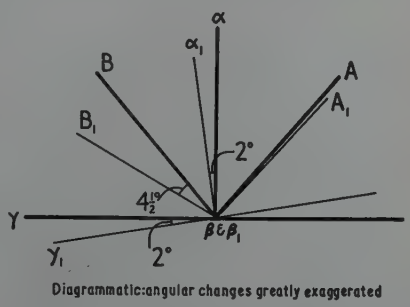


FIG. 3. Allivalite plagioclase: movement of indicatrix and of optic axes on heating. α and γ = indicatrix axes, A and B = optic axes before heating; α_1 and γ_1 = indicatrix axes, A_1 and B_1 = optic axes after heating.

Plagioclase from Juvinas. Table III also shows the changes, after heating, in the twin-angle values; unfortunately only two grains with Carlsbad twins could be remeasured. The measurements made on grains with albite-Carlsbad twins have been omitted since no comparison with the allivalite plagioclase is possible. The changes that occur on heating are more variable

than those that took place in the allivalite plagioclase. Some crystal show virtually no change after heating (e.g. grain 2 of the albite twin and one grain having an albite-Carlsbad twin). Others show change comparable with those which occurred in the allivalite plagioclase (e.g. grain 7 of the albite twins). The much reduced mean change in BB_1 is of course, mainly due to the generally smaller increase in 2V compared with its increase in the allivalite felspar.

Owing to the smallness of the sample it is not possible to determine which crystals are unaffected by heating and which are most affected; in other words it is impossible to relate the change to the composition of the crystal (as indicated by the value of 2V). Different crystals belonging to the 'main group' (p. 659) showed both maximum and minimum change. Such as it is, the evidence does not point to a correlation. Unfortunately none of the crystals belonging to the much smaller, more sodic 'tail' (p. 659) could be measured both before and after heat treatment.

Finally, under the results of heat treatment, reference must be made to the homogenizing effect on twinned Juvinas plagioclases, in which the two twin-members, before heating, were of presumably different composition. Evidence for this is given by the prevalence of triangles of error in the location of the twin-axes at the intersection of great circles through $\alpha\alpha_1$, $\beta\beta_1$, and $\gamma\gamma_1$. Thus nine of the ten albite twinned Juvinas crystals listed in table III, before heating, gave triangles of error. After heating the triangles were, in every instance, reduced in size—in five instances almost to vanishing point. The allivalite plagioclases seldom gave triangles of error for the twin-axes before heating. The few exceptions (small triangles) were unaffected by the heat treatment.

Twin-law frequencies for Juvinas plagioclases. Determination of the twin-laws on 111 crystals (randomly located in two thin sections) gave the following percentage frequencies: albite 33 %, Carlsbad 18 %, albite-Carlsbad 25 %, pericline (and acline) 11 %, Manebach 9 %, Baveno 3 % (2 % 'right', 1 % 'left'), albite-Ala 1 %, Ala < 1 %. Virtually all types of twinning are, therefore, present in Juvinas plagioclases, but albite, Carlsbad, and albite-Carlsbad twins represent more than three-quarters of the total.

Of ten 'threelings' which were measured, five showed combinations of albite and Manebach or Carlsbad and Manebach twins. The remaining five showed combinations of albite and Carlsbad, albite and pericline, Carlsbad and pericline, and albite-Carlsbad and pericline twins. One of two 'fourlings' showed an albite-Ala association; the other showed a combined albite, Carlsbad, and albite-Carlsbad twin.

Specific gravities. A sample of approximately 3 000 grains of each plagioclase was placed in the diffusion column during the period in which a linear relationship existed between height and specific gravity.

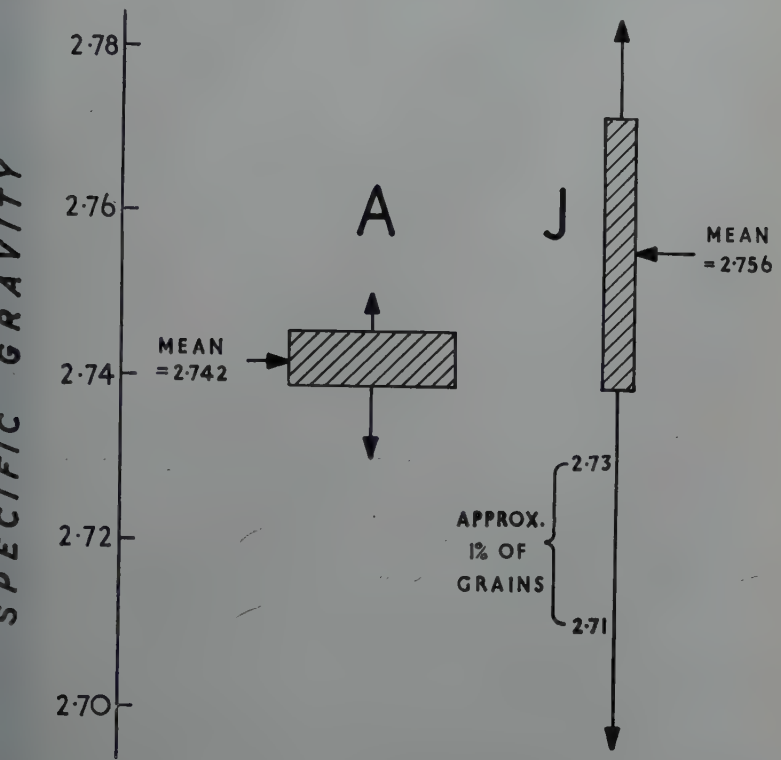


FIG. 4. Specific gravity ranges: A = allivalite; J = Juvinas. The main layer is shown shaded. The arrows indicate the extensions of the scattered grains above and below the main layer. The rectangles are of equal area, denoting approximately equal numbers of grains. The difference between the means corresponds to a $7\frac{3}{4}$ % anorthite difference.

The allivalite felspar then formed a narrow, compact layer with scarcely any noticeable 'fringe'.

The Juvinas plagioclase, by contrast, formed a main layer five times as broad as the allivalite felspar layer and divided into coalescing zones. This 'main' layer showed 'fringes' of scattered grains, particularly on the upper side (lower sp.gr.). The specific gravity limits of the main layer and of the extensions above and below it are shown diagrammatically in fig. 4.

Optical examination of several of the plagioclases of abnormally lo gravity showed no inclusions, bubbles, &c., that could account for thes values. It was also found that their refractive indices were abnormall low (see p. 659). These results show that some plagioclase grains fro Juvinas are as sodic as $Ab_{35}An_{65}$, but the proportion of such grains hav ing a composition markedly different from the main mass is small an probably does not exceed 1 %.

TABLE IV. Chemical analyses of plagioclases from allivalite (B.M. 1923, 476, [21 and from the Juvinas meteorite (B.M. 90262); analyst: P. M. Game.

		1.	2.			1a.		2a.	
SiO_2	...	46·66	46·59	Si	...	8·643		8·662	15·9
Al_2O_3	...	33·40	33·42	Al	...	7·290	16·02	7·322	
Fe_2O_3	...	0·62	—	Fe···	...	0·087			
FeO	...	—	0·80	Fe··	...	—		0·124	
CaO	...	16·50	16·40	Ca	...	3·273		3·265	4·17
Na_2O	...	1·98	2·04	Na	...	0·711	4·02	0·735	
K_2O	...	0·16	0·20	K	...	0·038		0·047	
H_2O+	...	0·49	0·43	O	...	32·00		32·09	
		99·81	99·88	Molecular composition (see text):					
Sp. gr.		2·742	2·756	1. An 82·5, Ab 16·6, Or 0·9.					
				2. An 82·6, Ab 16·3, Or 1·1.					

1. Plagioclase from allivalite.
2. Plagioclase from Juvinas.

1*a*, 2*a*. Empirical unit-cell contents, calculated using the determined specif gravities and cell volumes interpolated from values given by W. F. Cole, H. Söru and W. H. Taylor: Acta Cryst. 1951, vol. 4, pp. 22 and 23 [M.A. **11**–427].

Composition. The results of the analyses of both plagioclases are give in table IV, and the unit-cell contents, derived therefrom, are also show The 4 % excess of alkalis in the unit cell of the Juvinas plagioclase mainl results from the inclusion of the FeO. No better balance can be obtaine in the lattice, however, by substituting this Fe″ for Al. It seems possib that part of this ferrous iron derives from minute pyroxene inclusions i the Juvinas felspar and should be regarded as an impurity. Subsequen microscopic examination with a magnification of about ×400 confirm the presence of numerous rod-like inclusions, width 1 to 4 μ, length 10 t 40 μ, often showing parallel orientation.

Since it was considered that SiO_2 was the most reliably determine oxide (three independent determinations for each plagioclase differed b only 0·1 %) the molecular compositions were derived as the means of th values obtained, on the one hand, from the SiO_2 percentages, and, on th other, from the ratio of CaO to total alkalis. A direct colorimetric com parison of the SiO_2 contents of the two plagioclases gave: SiO_2 (allivali

plagioclase):SiO_2 (Juvinas plagioclase) = 1·000:1·003. The difference is within the limits of experimental error. From this result and from the complete analyses the composition of the two plagioclases can thus be considered to be virtually identical. It is therefore surprising to find that independent optical properties and specific gravity values consistently indicate an anorthite content for the Juvinas plagioclase higher by 6 to 7 % than that for the plagioclase of the allivalite.

In table V the mean values, the difference in these means, and the

TABLE V. Compositional differences in Juvinas and allivalite plagioclases inferred from optical and specific gravity values.

		Mean value. Allivalite.	Mean value. Juvinas.	Difference between means.	Corresponding difference in anorthite percentage.
Refr. index (β) ...	...	1·5760	1·5790	0·0030	5¾ %
$2V_\alpha$	...	81·1°	78·0°	3·1°	6¾ %
Twin-angle (albite twins) $\alpha\alpha_1$	...	63½	66¾	3¼°	6% (mean)
Twin-angle (albite twins) $\gamma\gamma_1$	...	91¼	93¾	2½°	
Twin-angle (albite twins) BB_1	...	6¾	1¼	5½°	
Sp. gr.	...	2·742	2·756	0·014	7¾ %

corresponding anorthite percentage differences are given for three independent optical parameters and for the specific gravity. The anorthite differences were obtained by taking, from recently published data[1] relating optics and specific gravity to anorthite content, a mean figure for the rate of change at this composition.

A fraction of the indicated difference in anorthite content may be due to the greater range in composition of the Juvinas felspar, which, as shown on p. 668, includes a small percentage of plagioclase as sodic as $Ab_{35}An_{65}$. Optical determinations on somewhat limited samples might not have accorded true representation to this small proportion of grains of a different composition. Also the possible substitution, in the Juvinas plagioclase, of Ca atoms by about 4 % of Fe″ atoms, of smaller ionic radius and greater mass, might be expected to have some influence on the lattice, and to raise the specific gravity and possibly the refractive

[1] G. C. Kennedy, Amer. Min., 1947, vol. 32, p. 562, fig. 1 [M.A. **10**-267]; F. Chayes, Amer. Journ. Sci., 1952, Bowen vol., pt. 1, p. 96, table 5 [M.A. **12**-134]; R. M. Crump and K. B. Ketner, Mem. Geol. Soc. Amer., 1953, no. 52, p. 31, fig. 6; A. N. Winchell and H. Winchell, Elements of Optical Mineralogy, 4th edn, 1951, pt. 2, p. 316; E. Wenk, Schweiz. Min. Petr. Mitt., 1945, vol. 25, p. 369, fig. 1; A. Poldervaart, Amer. Min., 1950, vol. 35, p. 1069, fig. 1 [M.A. **11**-389]; H. Tertsch, Tschermaks Min. Petr. Mitt., 1942, vol. 54, p. 206, fig. 4*a*, and p. 208, fig. 5*a* [M.A. **9**-270].

indices. However, X-ray powder photographs of the two felspar recorded with a camera of 11·46 cm. radius, showed no differences.

Discussion.

Twinning and composition. The twinning of the Juvinas plagioclas quite closely resembles that of the plagioclases of terrestrial basalts an allied types. Thus twin-law frequencies for the Juvinas plagioclase com pare as follows with the frequencies (in parentheses) for the plagioclase of 'basaltic' rocks, calculated from about 2 400 determinations made b six investigators:[1] albite, Carlsbad, and albite-Carlsbad 76 % (79·4 % pericline and acline 11 % (11·8 %), Manebach 9 % (5·1 %), Baveno 3 % (1·4 %), albite-Ala 1 % (1·6 %), Ala < 1 % (0·7 %).

It is not easy to account for the frequent differences between con tiguous twin lamellae of the Juvinas plagioclase. Although such di ferences have often been noted in the intermediate plagioclases, the presence in bytownites and anorthites is rare. In such calcic plagioclas according to R. C. Emmons and V. Mann,[2] a very small or negligib compositional difference is the rule. It is possible that these differenc (derived from optical measurements) are caused by strain and have n chemical foundation. Strains have certainly affected the meteorite, a shown by the discontinuous twinning and 'patchy' extinction of son of the felspars.

An alternative explanation is that the twinning may have replace original zoning so that, as Emmons and Mann believe, 'the difference i composition of contiguous twin lamellae, in part at least, substitutes fo the difference in composition between zones'. In view of the compos tional range recorded in the Juvinas plagioclase, the likelihood of origin zoning seems high; indeed, traces of it still remain. The elimination these differences on heating is probably due to the greater molecul diffusion at these relatively high temperatures.

The compositional range supports a theory of formation by cryst settling in a differentiating magma.

Cooling conditions. Inferences on the thermal history of the Juvina

[1] C. T. Barber, Mem. Geol. Surv. India, 1936, vol. 68, pt. 2, p. 224, table 6 [M. 7–21]; M. Gorai, Amer. Min., 1951, vol. 36, p. 885, table 1 [M.A. 11–489]; W. Lar son, Bull. Geol. Inst. Univ. Upsala, 1941, vol. 28, p. 373 [M.A. 9–177]; G. Paliu Schweiz. Min. Petr. Mitt., 1932, vol. 12, p. 428 [M.A. 5–436]; W. R. Chapma Amer. Min., 1936, vol. 21, p. 39, table 2 [M.A. 6–293]; A. Vendl, Tschermaks Mi Petr. Mitt., 1931, vol. 42, pp. 491–550; Vendl's results summarized by H. Wieser der, ibid., 1933, vol. 44, p. 203.

[2] Mem. Geol. Soc. Amer., 1953, vol. 52, p. 42.

lagioclase must depend upon a comparison between the results of the eating experiments on this felspar on the one hand and on the plagio-lase from the Rhum allivalite on the other.

The bytownite from the Rhum allivalite can be assumed to have rystallized from the magma at a high temperature and to have cooled xtremely slowly. In fact, G. M. Brown[1] has shown that there was little ecrease of temperature during the lengthy period of deposition of 2600 eet of the 'layered series'.

Although P. Gay[2] was unable to detect any difference in the X-ray owder pattern of this plagioclase after 3 days' heat treatment at 100° C. it has been shown that 2 days' heating at 1100° C. did, in fact, roduce small but significant optical changes which showed considerable onstancy in size and direction; these optical changes are probably aused by movement in the calcium (and sodium) ions only; the X-ray vidence suggests that higher temperatures (about 1300° C.) are needed o bring about disordering of the Si-Al distribution. The relatively rapid oling of the artificially heated allivalite did not allow complete rever-al of the structural change in its plagioclase, whereas it seems reasonable o believe that the very slow natural cooling of this same felspar did ermit a complete return to its original structural state; it is thus the otally different order of the cooling rates that is responsible for the tructural (and therefore optical) differences. Had it proved possible to epeat Nature's extremely slow cooling, the allivalite plagioclase would resumably have emerged from the heat treatment unaltered.

The plagioclase from Juvinas, after identical heat treatment, behaved fferently, at least in part. In the first place some grains showed no otical change after heating. Secondly the changes that did occur varied om grain to grain both in magnitude and in direction. Those Juvinas agioclases that showed no change after heating must be assumed to ave been subjected to previous natural quenching; repetition of the rlier, natural cycle would then be expected to leave the final structure naltered. Other crystals presumably underwent slower cooling; in a w, which showed changes comparable with those in the allivalite plagio-ase, the cooling may have been slow and uninterrupted.

Acknowledgements. I am grateful to Dr. A. A. Moss and Mr. D. I. Bothwell for vice and help in various analytical methods. I also wish to thank Mr. H. G. ven for developing the method of heating thin sections, and Mr. R. T. W. Atkins drawing the figures.

[1] Phil. Trans. Roy. Soc., 1956, ser. B, vol. 240, p. 48.

[2] Min. Mag., vol. 30, 1954, table 1, p. 433.

Saponite from Allt Ribhein, Fiskavaig Bay, Skye.

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[Read 1 November 1956.]

Summary. This saponite, which is closely associated with zeolites such as stilbi heulandite, thomsonite, and gonnardite, occurs in vesicles in basalt. It has t composition: $1{\cdot}02M^{+}$ $(Mg_{5{\cdot}84}Mn_{0{\cdot}01}Al_{0{\cdot}03}Fe_{0{\cdot}08})$ $(Si_{6{\cdot}99}Al_{1{\cdot}01})O_{20}(OH)_4$, according t new method for calculating the ionic formulae of smectites: this method a enables determination of the temperature at which all sorbed moisture is removed in this instance about 800° C. The exchangeable cations are largely Ca^{2+}. The cher cal, thermal, and X-ray data are discussed with reference to other saponite sampl Electron-microscope examination showed a tendency to elongation in the direct of the *a*-axis. It is concluded that the saponite is of excellent purity and free fr interstratification.

A VEIN of very pale blue, almost white, saponite was exposed d ing excavation of a water dam in Skye: this vein was said to 5 to 6 feet long, about 1 foot deep, and up to 2 inches thick. Since t site is now covered with concrete, no more bulk material is availab however, some small pieces have recently been recovered from the sp heap by Mr. R. H. S. Robertson.

The locality of the vein is on the small stream Allt Ribhein (m reference on the Ordnance Survey Popular Edition 1 inch map, sheet 3 635545), which flows into Fiskavaig Bay, on the south side of Lo Bracadale. It is in an area of Skye where the lavas are notoriously ve cular. In the immediate neighbourhood of the dam the lava is cut only by a sill, but also by a dyke. Some of the rock excavated was in advanced state of decay, but this process of deep-weathering does seem to account for the saponite.

The vesicles in the lava are often as much as 2 cm. in diameter. Th may be filled with white zeolites (stilbite, heulandite, and thomson have been identified at this locality) or with saponite, or they may h an inner core of saponite surrounded by a rim of zeolite, which in t samples examined was largely gonnardite. From the evidence availa it appears that the saponite was formed *after* and in a manner exac similar to the more common zeolitic infillings. The contents of amygdules have obviously been carried into the cavities dissolved

water, which may itself have been of volcanic origin (see Harker and Clough, 1904).

Optical data. The saponite occurs in fan-shaped aggregates (fig. 1) rather similar to those described by Konta and Šindelář for the saponite from Čáslav. The optical data together with those for some other recently-described saponite samples are given in table I. The γ value is

FIG. 1. Photomicrograph of saponite, Allt Ribhein, Skye.

somewhat higher than those quoted by Winchell (1951) for several low-iron saponites, but is similar to that for the Čáslav sample which has a fairly high iron content; values may, however, vary with the water content and with the exchangeable cation. The γ-index is parallel to the direction of elongation and the α is perpendicular to the principal cleavage plane. From electron-microscope data α corresponds to the direction of the c-axis, β to the b-axis, and γ to the a-axis.

Chemical data. The chemical analysis of a Ca-saturated sample is compared with some published analyses in table I. The two Skye samples are very similar in composition. The cation-exchange capacity of the Allt Ribhein material is 109 m.e. per 100 g., the exchangeable cations in the natural sample being about 92% Ca^{2+} and 8% Mg^{2+}. Several

analyses given by Heddle (1879, see Harker and Clough, 1904) appear from their high CaO content, also to refer to essentially Ca-saturated material, but it is doubtful whether the Quirang sample was pure as the CaO content is considerably higher than would be expected for a sample of normal cation-exchange capacity and the Na_2O content is also high.

TABLE I. Chemical analyses and optical data for saponite.

	1.	2.	3.	4.	5.	6.
SiO_2	43·62	42·50	53·88	50·01	54·74*	40·46
TiO_2	0·00	—	0·25	<0·04	—	—
Al_2O_3	5·50	5·06	4·47	3·89	8·93*	10·15
Fe_2O_3...	0·66	0·85	0·60	0·21	0·43*	3·56
FeO	—	—	—	—	—	4·89
CaO	2·85	3·27	—	1·31	2·65*	1·94
MgO	24·32	23·95	31·61	25·61	33·28*	20·71
MnO	0·06	0·22	—	—	—	0·24
Na_2O	0·08	0·45	0·01	—	—	0·25
K_2O	0·04	0·17	0·05	—	—	0·32
$H_2O-105°$ C. ...	—	15·52	9·28	7·28	—	13·33
$H_2O-300°$ C. ...	17·42	—		—	14·09	—
H_2O+	5·48	8·16		12·02	5·01	4·24
Σ	100·03	100·15	100·15	100·37	—	100·23
α	1·490	—	—	1·511	—	1·513
β	1·531	—	1·486 to 1·493	—	—	—
γ	1·534	—	—	1·514	1·498	1·536
$\gamma-\alpha$	0·044	—	—	0·003	0·004 to 0·007	0·023

1. Allt Ribhein, Skye. (Anal. J. B. Craig).
2. Quirang, Skye (Heddle, 1879).
3. Krugersdorp, Transvaal (Schmidt and Heystek, 1953).
4. Milford, Utah, U.S.A. (Cahoon, 1954).
5. Groschlattengrün, Germany (Weiss, Koch, and Hofmann, 1955).
6. Čáslav, Czechoslovakia (Konta and Šindelář, 1955).

* Determined on ignited weight.
† 160° C. ‡ Includes P_2O_5 0·14.

it may, therefore, have been contaminated with zeolites. The preponderance of exchangeable Ca^{2+} is paralleled in the zeolitic infillings, which usually consist of lime or soda-lime zeolites with lime as the principal base (Harker and Clough, 1904).

The usual method of calculating the smectite structural formula is that of Ross and Hendricks (1945), based upon the assumption that each structural unit contains 20 oxygen and 4 hydroxyl ions giving it a total negative valency of 44. No account is taken of the measured H_2O- content. On this basis the saponites for which analyses were quoted in table I have the formulae indicated in table II (*a*).

An alternative method of calculation of the structural formula using the measured H_2O+ content may be derived by modifying the calculation of Brown and Norrish (1952) for the hydrous micas. If one assumes the oxygen and water contents obtained by analysis to be divided up according to the proportions 20 O^{2-}:4 OH^-:x H_2O, where xH_2O is the

TABLE II. Ionic formulae for saponites (reference nos. see table I).

(*a*) By the method of Ross and Hendricks (1945).

		1.		2.		3.		4.		5.		6.	
M^+	...	1·02		1·48		0·83		0·42		1·22		1·08	
Mg	...	5·82	5·95	5·87	6·00	5·96	6·00	5·74	5·88	5·90	6·00	4·70	6·00
Fe^{2+}	...	—		—		—		—		—		0·64	
Mn	...	0·01		—		—		—		—		0·02	
Al	...	0·04		0·03		—		0·12		0·06		0·22	
Fe^{3+}	...	0·08		0·10		0·02		0·02		0·04		0·42	
Ti	...	—		—		0·02		—		—		—	
Si	...	7·00	8·00	7·02	8·00	7·24	8·00	7·48	8·00	6·26	8·00	6·34	8·00
Al	...	1·00		0·98		0·72		0·52		1·24		1·66	
Fe	...	—		—		0·04		—		—		—	
O	...	20		20		20		20		20		20	
OH	...	4		4		4		4		4		4	

(*b*) By new method.

		1.		2.		3.		4.		5.		6.	
M^+	...	1·02		1·35		0·75		0·42		1·18		1·09	
Mg	...	5·84	5·96	5·86	5·89	5·98	6·00	5·75	5·95	5·91	6·00	4·72	6·00
Fe^{2+}	...	—		—		—		—		—		0·64	
Mn	...	0·01		0·03		—		—		—		0·03	
Al	...	0·03		—		—		0·17		0·05		0·19	
Fe^{3+}	...	0·08		—		—		0·03		0·04		0·42	
Ti	...	—		—		0·02		—		—		—	
Si	...	6·99	8·00	6·92	8·00	7·22	8·00	7·49	8·00	6·75	8·00	6·32	8·00
Al	...	1·01		0·97		0·71		0·51		1·25		1·68	
Fe	...	—		0·11		0·07		—		—		—	
O	...	20		20		20		20		20		20	
OH	...	4		4		4		4		4		4	

excess sorbed moisture not removed at 105° C. (or any other temperature that may be chosen), one can derive the equations:

$$n[O^{2-}] = 20+4+x \qquad (1)$$

and

$$n[H^+] = 4+2x, \qquad (2)$$

where n is the factor by which the ionic proportions of oxygen, $[O^{2-}]$, and hydrogen, $[H^+]$, obtained from the analysis must be multiplied to obtain the final formula. Combination of equations (1) and (2) gives:

$$2n[O^{2-}]-n[H^+] = 44. \qquad (3)$$

Using the values of n calculated from equation (3), the formulae in Table II (*b*) are obtained for the saponite samples previously referred to.

The Quirang and the Krugersdorp samples appear to require tetrahedra substitution of Fe^{3+}. However, since both appear to be virtually tru saponite end-members, any slight errors in analysis would be magnified in addition, the Quirang sample, as previously mentioned, was probabl impure. For the Krugersdorp saponite both methods of calculatio require a small amount of tetrahedral Fe^{3+}, the charge balance on th new basis is satisfactory, and the calculated cation-exchange capacit of 96 m.e. per 100 g. agrees with the measured value of 100 m.e. pe 100 g. (Schmidt and Heystek, 1953). Thus, it may be that the ver small octahedral Fe^{3+} content is true (cf. cronstedtite, which is believe to have considerable tetrahedral Fe^{3+}). In general the formulae obtaine by the two methods differ only in detail.

In addition to giving the structural formula, however, this new metho enables one to measure the amount of excess hygroscopic moisture in th H_2O+ content. Thus, from equation (1):

$$x = n[O^{2-}]-24$$

and

$$x/n \times 18 = \% \text{ excess moisture.}$$

For the Allt Ribhein sample the excess hygroscopic moisture in th H_2O+ figure is 1·74 %; thus, from the dehydration curve (fig. 3), th sorbed water would appear not to be completely removed below abou 800° C. This is in agreement with experiment, since the material heate to 750° C. rehydrates quite rapidly on exposure to the atmosphere. A similar calculation for the Čáslav sample indicates a temperature of abou 600–700° C. for complete removal of sorbed water.

This method of calculation has interesting possibilities for smectite since it should enable reasonably accurate determination of the tot sorbed water content, which is not readily measured experimentall Only by applying it to analyses of pure samples can it be checked, an for several known to the author it appears to give satisfactory result Many of the published analyses for smectites are, unfortunately, for in pure material from which little information of value can be derived.

X-ray and thermal data. The X-ray diffraction patterns were typic of a trioctahedral smectite, but contamination with a very small quan tity of coarse-grained zeolite was noted. The differential thermal curv is compared with those for some other saponites in fig. 2. It will be note that the curves fall into two distinct groups depending upon the presenc or absence of the peak at about 600° C. Weiss, Koch, and Hofman (1955) attribute this peak to the dehydroxylation reaction and the fin endothermic peak to the crystallization of enstatite from 'anhydr

saponite', but their interpretation is based upon X-ray results for material heated to above 700° C. for some 200 hours, a period much too long to give valid comparison with the differential thermal curve. Both the Allt

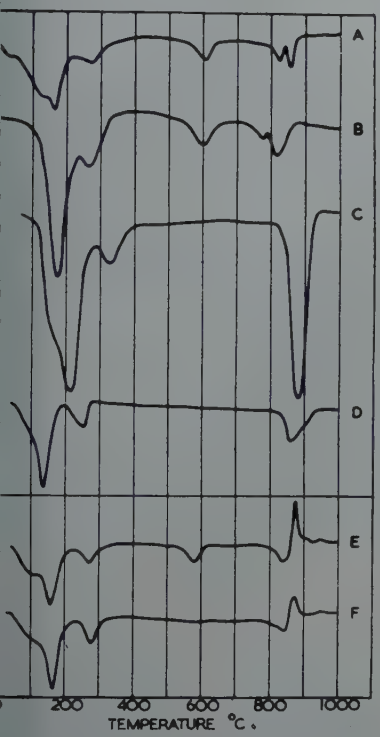


FIG. 2. Differential thermal curves for saponites (*A*—Cornwall, England; *B*—Groschlattengrün, Germany, after Weiss, Koch, and Hofmann, 1955; *C*—Krugersdorp, Transvaal, after Schmidt and Heystek, 1953; *D*—Allt Ribhein, Skye) and vermiculites (*E*—Kenya; *F*—West Chester, Pennsylvania, U.S.A.).

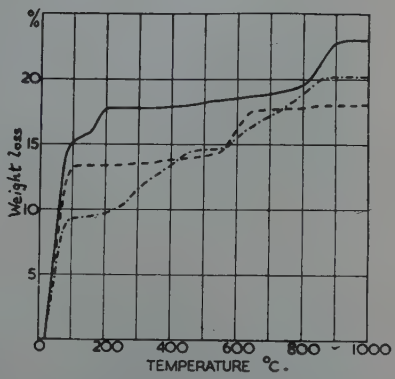


FIG. 3. Dehydration curves for saponite, Allt Ribhein, Skye (———); montmorillonite, Wyoming, U.S.A. (– – – – –); vermiculite, West Chester, Pennsylvania, U.S.A. (–·–·–·–).

Ribhein material and the Cornwall sample when heated to 700° C. in the differential thermal apparatus give the X-ray pattern of talc: dehydroxylation does not therefore occur until about 800–900° C., and the final peak must represent this reaction. Crystallization to enstatite probably occurs simultaneously. This mechanism is confirmed by the dehydration curve in fig. 3.

Comparison of the saponite dehydration curve with those for mon morillonite and vermiculite (fig. 3) shows that dehydroxylation occurs a a higher temperature than that of montmorillonite, and that the curv shows much sharper breaks between the various phases of water lo than that for vermiculite.

It seems, therefore, that the attribution of the 600° C. peak remains t be explained. Cole and Hosking (1957), after considering the structura similarity of saponite, vermiculite, and chlorite, suggest that saponi and chlorite may, like vermiculite and chlorite, form random inte growths that are difficult to detect by X-ray examination, but are readil detected by differential thermal analysis. They attribute the 600° C peak, therefore, to interleaved chlorite. It would not require many inte leaved brucite layers to give rise to a chlorite peak of the size observe on curves *A* and *B*—cf. the effect of interleaved brucite layers on th vermiculite curve (curves *E* and *F*, fig. 2). X-ray examination of th Cornish material showed a very small amount of kaolinite contamina tion, but this does not seem sufficient to give a peak of the magnitud observed. The doubling of the final peak supports the suggestion of Co and Hosking (1957), since magnesian chlorites give a strong exotherm peak in the 800° C. region and this superposed on a single endotherm peak would give an impression of doubling. Pronounced doubling only observed with samples giving the 600° C. peak.

It seems highly probable, therefore, that the Cornwall and Grosch lattengrün 'saponites' are in reality interstratified chloritic-saponite and the Allt Ribhein and Krugersdorp (as well as the Čáslav) samples ar true saponites. The initial part of all these curves is, of course, a func tion of the exchangeable ion and pretreatment: the slight doubling of th second peak on curve *D*, fig. 2, may be due to the small amount of mag nesium present (Mg-saturated material gives a peak at about 275° C and Ca-saturated at about 260° C.).

Electron-microscope data. Electron-microscope examination showe the saponite to be platy with a notable tendency to elongation (figs. 4 5*a*), some thin crystals being apparently folded over at right angles i the manner observed by Cahoon (1954) for the Milford material (fig. 4). Single crystal electron-diffraction patterns (fig. 5*b*) showed the elongatio to occur uniformly in the direction of the *a*-axis, and gave the cell dimensions $a = 5{\cdot}3$ Å., $b = 9{\cdot}2$ Å. This value for the *b*-axis compare well with the value of 9·21 Å. calculated theoretically from the composi tion by the formula of Brindley and MacEwan (1953).

Conclusion. The Allt Ribhein material would thus appear to be a

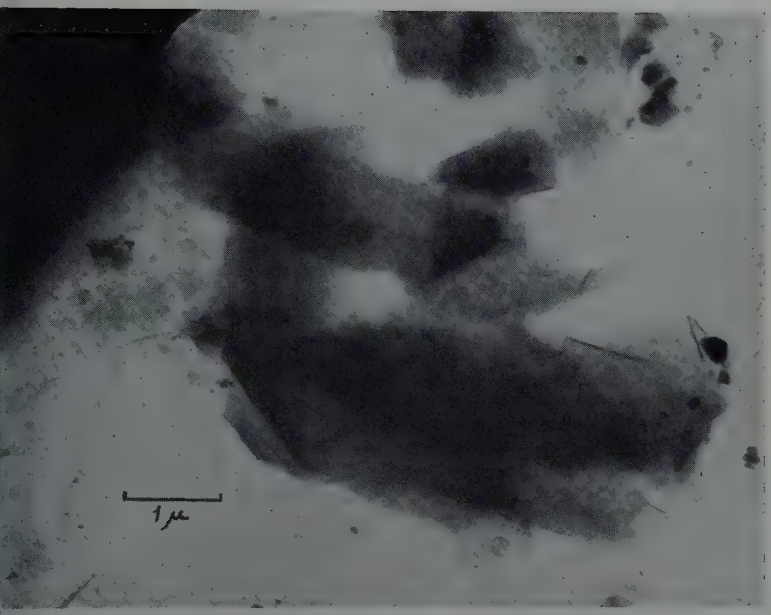
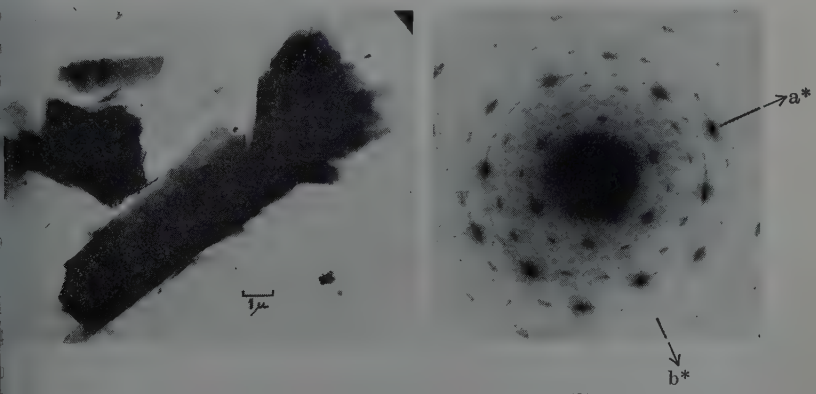


FIG. 4. Electron micrograph of saponite, Allt Ribhein, Skye.



(*a*) (*b*)

G. 5. Electron micrograph (*a*) and electron-diffraction pattern (*b*) of saponite, lt Ribhein, Skye. Same crystal in same orientation used for both photographs.

good saponite of low iron content and free from interstratification; it occurs in platelets elongated along the *a*-axis. It is probable that the material from Quirang described by Heddle was similar.

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The illite in some Old Red Sandstone soils and sediments.

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[Read 24 January 1957.]

Summary. An illite separated from an Upper Old Red Sandstone sediment at Denholm Hill Quarry, Roxburghshire, when examined by optical, X-ray, and chemical methods, appeared to be closely similar to Fithian illite. Its composition was $\cdot 96\, M^{+}(Al_{2\cdot 86}Fe^{3+}_{0\cdot 31}Fe^{2+}_{0\cdot 09}Mg_{0\cdot 68})(Si_{6\cdot 92}Al_{1\cdot 08})O_{20}(OH)_4$, where M^{+} for the Ca-saturated sample was $[(H_3O)_{0\cdot 58}Ca_{0\cdot 10}Na_{0\cdot 06}K_{1\cdot 12}]$. The differential thermal curve showed two peaks: one at 550° C. and the other at 600° C. (i.e. somewhat intermediate between the Fithian and Ballater illites). The dehydration curve was also intermediate. Electron-microscope examination showed rather better crystallization than in Fithian illite. The possible reasons for variation of the illite peak temperature are discussed.

EARLIER thermal studies have shown that the illite in soils developed on Old Red Sandstone till is 'abnormal', in the sense that the main endothermic peak on the differential thermal curve is at 580–600° C. instead of at 550° C. (Mackenzie, 1954, 1956); the peak is thus not additive with the kandite one and the curve obtained for such soil-clays is reasonably characteristic (fig. 1).

It has also been noted that the soils derived from Upper Old Red Sandstone in Roxburghshire differed from those derived from Middle Old Red Sandstone material in Aberdeenshire in that the 580–600° C. peak is less sharply defined (and perhaps rather smaller) for the former than for the latter (cf. figs. 1*a* and 1*b*). The reason for this difference is not known; it might be due to different weathering conditions, or, if the illite is inherited from the parent rock, to differences in the age or the parent material of the sediment.

The fact that this type of illite has so far been observed only in soils derived from the Old Red Sandstone formation suggested that the illite was inherited from the rock; examination of the clay fraction of several samples of Old Red Sandstone sediments confirmed this view. One of the samples so examined—namely, one from Denholm Hill Quarry, Roxburghshire, grid reference NT/572171—had an illite content of about 90% and it was found possible to purify this sample by size fractionation

using sedimentation and the Sharples supercentrifuge. Thus, th 0·4–0·2 μ fraction appeared from X-ray examination to be pure illi with only a trace of kandite and with some contaminating iron oxid the $< 0{\cdot}2$ μ fraction also appeared relatively pure, although some sca tering at low angles rendered this less certain. On removal of free iro oxide from the 0·4–0·2 μ fraction by the method of Mitchell an Mackenzie (1954) a creamy-coloured illite of excellent purity w obtained.

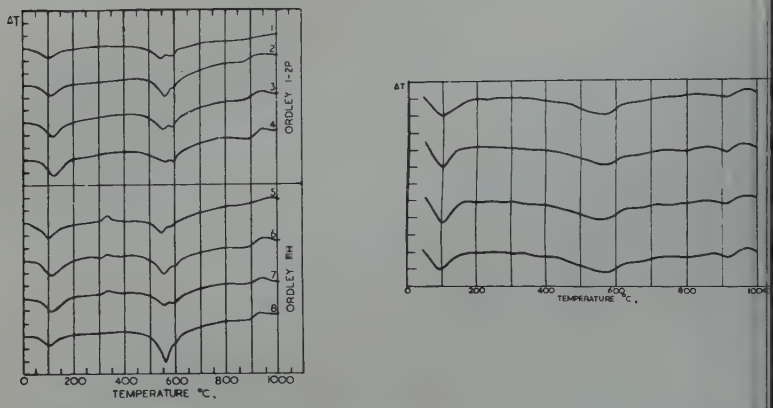


Fig. 1. Differential thermal curves for clays from soils developed on till derived fr Old Red Sandstone sediments: (*a*) Middle Old Red Sandstone, Ordley, Aberde shire (1–2 P, freely drained; PH, poorly drained); (*b*) Upper Old Red Sandsto Belling Hill, Roxburghshire.

X-ray data. The spacings obtained from the X-ray powder diffra tion pattern are given in table I, together with, for comparison, those f single-layer, monoclinic (1M) illite, disordered 1M (1M*d*) illite (Levinso 1955), and illite from Fithian, Illinois, U.S.A. From these data it will seen that both the Denholm Hill and the Fithian samples examined a dioctahedral illites and satisfy the criteria given by Levinson (1955) f the 1M*d* structure. The lattice parameters for the Denholm Hill mater are $a = 5{\cdot}16$ Å., $b = 9{\cdot}02$ Å., $c = 9{\cdot}99$ Å.

Thermal data. Since the X-ray examination revealed no obvious d ferences between the Denholm Hill and the Fithian illites, the therm data are of considerable importance. It is particularly interesting th removal of the kandite from the total clay fraction (curve *A*, fig. 2) d not remove completely the 550° C. peak (curves *B* and *C*, fig. 2)—a this peak is too large to be attributed to the trace of kandite remainin

Thus, the illite does not have a single peak at about 600° C., as was originally envisaged, but has a double peak system with one peak at 550° C. and the other at 600° C. In the 0·4–0·2 μ fraction both peaks are about the same size, but in the $< 0{\cdot}2$ μ fraction the first peak is larger

TABLE I. X-ray data for illites.

1M illite.*		1M*d* illite.*		Fithian.		Denholm Hill.	
d, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*
0·1	vs	10·1	s	10·2	vs	10·14	vs
4·98	m	4·98	w	4·98	m	4·98	w
4·50	s	4·48	s	4·49	s	4·50	vs
4·35	vw	—		—		—	
4·10	vw	—		—		4·12	vvw
3·85	vw	—		3·90	vvw	—	
3·62	ms	—		3·73	vvw	3·72	vvw
—		—		3·52	vw	3·53	vvw
3·32	s	3·33	s	3·34	ms	3·33	vs
3·08	ms	3·07	vw	3·01	w	2·99	vvw
2·89	mw	2·85	vw	2·87	vvw	—	
—		—		2·80	vvw	2·81	vw
2·67	w	—		—		—	
2·57	vs	2·57	vs	2·58	s	2·58	vs
2·47	w	2·46	w d	2·46	w	2·44	vvw
2·38	m	2·38	w d	2·395	mw	2·40	vw
2·25	mw	2·25	w d	2·253	vw	2·255	vvw
2·14	m	2·14	w d	2·145	m	2·136	vvw
1·99	s	1·99	w d	1·995	w	1·992	m
—		—		—		1·891	vvw
1·71	vw	—		1·703	w	1·702	vvw
1·65	m d	1·65	w d	—		1·647	vvw
1·58	vvw	—		—		—	
1·50	s	1·50	s	1·505	ms	1·504	m
—		—		—		1·453	vvw
1·38	vvw	—		—		—	
1·34	w d	1·34	w d	—		1·344	vvw
1·30	m	1·30	mw	1·295	m	1·293	vw
1·25	w	1·25	w	—		1·250	vw

* After Levinson (1955); 1M illite, St. Austell, Cornwall; 1M*d* illite, Fithian, Illinois, U.S.A.

than the second, with the result that this curve is nearer to that for the Fithian illite (curve *D*, fig. 2). In the coarse fraction containing the bulk of the kaolinite it would be expected, therefore, that the illite 600° C. peak would be slightly larger than the 550° C. one. Thus, there appears to be a variation in the ratio of the size of the two peaks, a conclusion which helps to explain this difference in the soil clays referred to in fig. 1, since it might be considered that the Aberdeenshire soil contained an

illite with a better defined and larger 600° C. component. An X-ra photograph with normal exposure taken after heating the illite t 575° C. (i.e. beyond the first peak) showed no difference in the diffractio pattern, either in position or in intensity of the lines, thus confirmin that the two peaks belong to the same material.

The dehydration curve shows no definite break corresponding to d hydroxylation in two steps, unless the inflexion commencing at abo

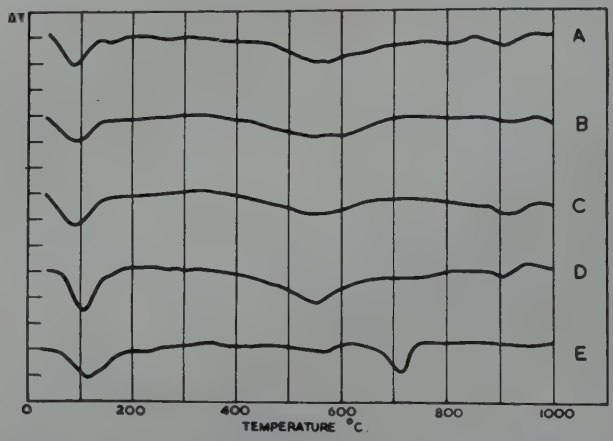


FIG. 2. Differential thermal curves for: *A*, total clay fraction of Old Red Sandsto rock, Denholm Hill, Roxburghshire; *B*, deferrified 0·4–0·2 μ fraction of san *C*, deferrified $< 0{\cdot}2\,\mu$ fraction of same; *D*, illite Fithian, Illinois, U.S.A.; *E*, illi Ballater, Aberdeenshire. (Curve *E* after Mackenzie, Walker, and Hart, 1949.

300° C. represents the first (fig. 3). This is not improbable, as the nea equilibrium nature of the dehydration curve lowers all temperatures about 100° C., at least, compared with the differential thermal curve.

From the appearance of both the differential thermal and the dehydr tion curves the Denholm Hill illite appears to be somewhat intermedia between the Fithian and the Ballater illites.

Optical data. The optical data, together with those for some oth illite samples, are given in table II. The Fithian illite may have be either the 2M or the 1M*d* polymorph, while the South Wales and t Ballater illites have the 1M*d* and 3T structures, respectively (Levinso 1955). The Denholm Hill material was biaxial negative and appea optically to be virtually identical with Fithian illite, bearing out t close similarity revealed by other data.

Chemical data. The chemical composition, as indicated by the analy

and the ionic formula calculated by the method of Brown and Norrish (1952) (table III), is also remarkably similar to that of Fithian illite. The cation-exchange capacity of 23·2 m.e. per 100 g. is virtually identical with that of the Fithian material of 23·5 m.e. per 100 g. Thus, the only significant difference is the iron content: the difference in CaO content is due to

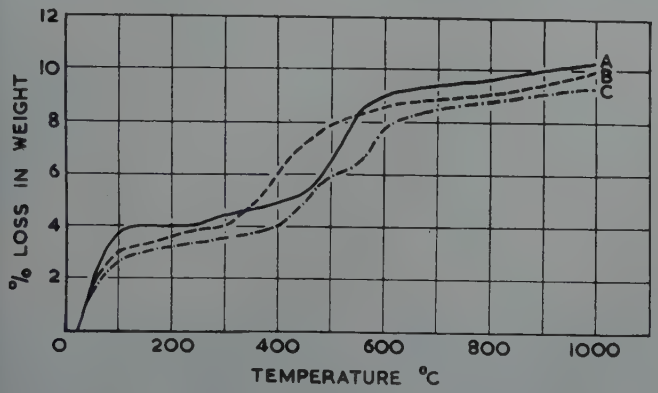


Fig. 3. Dehydration curves for illites from: *A*—Denholm Hill, Roxburghshire; *B*—Fithian, Illinois, U.S.A.; *C*—Ballater, Aberdeenshire.

Table II. Optical data for illites.

	1.	2.	3.	4.
α	1·555	1·555	1·572	1·568
β	1·571	—	1·587	1·590
γ	1·586	1·588	1·600	1·593
$\gamma-\alpha$	0·031	0·033	0·028	0·025
2 V	very small	small	small	large*

1. Denholm Hill Quarry, Roxburghshire.
2. Fithian, Illinois, U.S.A (after Grim, Bray, and Bradley, 1937).
3. South Wales (after Nagelschmidt and Hicks, 1943).
4. Ballater, Aberdeenshire (after Mackenzie, Walker, and Hart, 1949).

* Re-examination revealed an error in the original measurement.

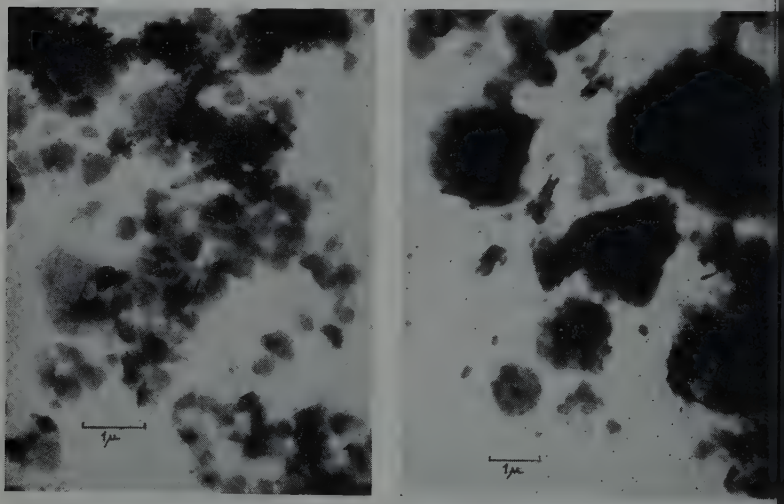
the fact that the Denholm Hill material was Ca-saturated before analysis. The South Wales illite, however, has an even lower iron content (Nagelschmidt and Hicks, 1943) than the Denholm Hill sample and yet gives a peak at 550° C. (Mackenzie, Walker, and Hart, 1949); it seems therefore that the difference between the thermal reactions of the Denholm Hill and Fithian illites cannot be explained on a compositional basis.

The lattice parameter *b* calculated from the composition by the method of Brindley and MacEwan (1953) is 9·03 Å., compared with the value of 9·02 Å. derived from the X-ray data.

TABLE III. Chemical data.

	Fithian.*	Denholm Hill.†		Ionic formula. Fithian.		Denholm Hill.	
SiO_2 ...	51·22%	49·85%	H_3O^+ ...	0·76	1·88	0·58	1·96
TiO_2 ...	0·53	0·62	Ca/2 ...	0·06		0·20	
Al_2O_3 ...	25·91	24·16	Na ...	0·04		0·06	
Fe_2O_3 ...	4·59	2·96	K ...	1·02		1·12	
FeO ...	1·70	0·80					
CaO ...	0·16	0·65	Si ...	6·75	8·00	6·92	8·00
MgO ...	2·84	3·27	Al ...	1·25		1·08	
MnO ...	—	tr.					
Na_2O ...	0·17	0·21	Al ...	2·77	3·97	2·86	3·94
K_2O ...	6·09	6·31	Fe^{3+} ...	0·45		0·31	
H_2O+ ...	7·14	6·22	Fe^{2+} ...	0·19		0·09	
H_2O- ...	—	4·75	Mg ...	0·56		0·68	
Σ	100·35	99·80					

* After Grim and Rowland (1941). † J. B. Craig, analyst.



(*a*) (*b*)

FIG. 4. Electron micrographs of illites: (*a*) Denholm Hill, Roxburghshire; (*b*) Fithian, Illinois, U.S.A.

Electron-microscope data. The Denholm Hill illite, under the electron microscope (fig. 4*a*), appears to be rather better crystallized than the Fithian material (fig. 4*b*), crystals of which have rather indeterminate fluffy edges. Shadow-casting showed both samples to consist of very thin platelets (about 200–400 Å. thick, or less).

Discussion. The data presented show that the illite from Denholm Hill, which, so far as is known, is the only illite as yet separated in a virtually pure state from Old Red Sandstone sediments, differs significantly from the Fithian material only in its thermal reaction. Since this difference cannot be associated with compositional differences it must be micro-structural, but it must be sufficiently slight not to show up on the X-ray diffraction pattern.

The thermal data, in effect, indicate that *some* of the hydroxyl groups of the illite are more tightly bound than in the normal type—i.e. they require a greater energy input before they can condense to evolve water. The most straightforward mechanism for this seems to be the following.

In the dioctahedral series only two out of every three octahedral positions are filled, and these positions are not all equivalent with respect to the hydroxyl groups in the oxygen–hydroxyl sheets above and below. It might be considered, therefore, that in a normal illite, such as the Fithian material, the octahedral ions are distributed largely around the oxygen ions and away from the hydroxyl ions. On the other hand, in Ballater illite, which may be regarded as the other end-member, the octahedral ions are distributed largely around the hydroxyl ions giving a tendency to stronger binding and in addition perhaps necessitating an alteration in the position of the octahedral ions before the hydroxyl groups on opposing sheets can condense. The greater energy required for such a system is reflected in the higher peak temperature for the dehydroxylation peak. The Denholm Hill material seems to be intermediate, in that part, roughly half, of the octahedral ions are in the positions occupied in normal illite while the remainder are rather more closely associated with hydroxyl groups—although not so closely associated as in Ballater illite. The two different arrangements could quite easily occur in the same sheet, and interlayering of sheets of two different types is not necessary. This view would tend to be supported by the X-ray evidence for the material heated to 575° C. Variation in the relative positions of the oxygen-hydroxyl sheets above and below the octahedral ions might also influence the result. No information regarding this hypothesis could be obtained from infra-red absorption spectra since the bands which would be affected were outside the range studied. The infra-red spectrum was, with small differences that cannot at present be definitely explained, similar to that for Fithian illite. No comparable system could operate with trioctahedral minerals, and it is significant that trioctahedral minerals, in which octahedral ions are necessarily in close contact with hydroxyl ions, generally have a much higher

dehydroxylation temperature than their dioctahedral analogues (c saponite and montmorillonite).

The arrangement visualized above is somewhat similar to that propose by Jonas and Grim (1957) to explain lowering of the peak temperature montmorillonite on rehydroxylation, and can equally be used to explai the existence of the 'normal' and 'abnormal' montmorillonites of Co (1955). It seems preferable to the vague 'order-disorder' suggestion Cole (1955)—who may, however, have had something of this nature i mind (see Cole and Hosking, 1957)—and in addition does not requi the corollary that normal illites alter to abnormal montmorillonites ar vice versa (Cole and Hosking, 1957). This corollary is particularly dif cult to justify for Ballater illite since it tends to contradict field evidenc

The only other illite known to the author which gives a peak at abo 600° C. is that described by Carr, Grimshaw, and Roberts (1953) fro some fireclay deposits, but for this material the peaks appear to be slightly higher temperatures. The reason for the shift is presumably t same as in the Denholm Hill material, but the illite is a 2M polymor and the chemical composition is quite different from that of the samp now described. The reason why this structure should form, so far as known, only in Old Red Sandstone sediments and in some fireclays is n clear. It suggests that the prevailing conditions imposed a certain stru tural order upon the clay mineral being formed, or that the prima minerals in the parent material of the sediments played a significant pa (since the fireclay illite occurs in fairly large sheets its structure m easily reflect that of a mica from which it was formed). Further work at present in progress to investigate how widespread is the occurrence this illite in Old Red Sandstone sediments, and whether it occurs in t Lower as well as the Upper and Middle beds. A differential therm curve for a clay from a Devonian deposit in Russia (Frank-Kamen sky, 1954) appears to show only one peak at about 550° C., althou in the absence of the peak tip it is difficult to be sure.

Acknowledgements. The author desires to thank Miss W. Smith, Mr. W. A. Mitch and Dr. V. C. Farmer of the Macaulay Institute and Dr. J. A. Gard, Chemis Department, University of Aberdeen, for the optical, X-ray, infra-red, electron-microscope data, respectively.

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Sapphirine-bearing rocks from MacRobertson Land, Antarctica.

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[Taken as read 7 November 1957.]

Summary. A small isolated outcrop in a large area of charnockites in the Mawso area, MacRobertson Land, Antarctica, consists of enstatite–sapphirine–cordieri rocks. Other highly magnesian outcrops occur in the district and these rocks ma be completely recrystallized xenoliths. Analyses of the country rock, the tw sapphirine-bearing rocks, and the sapphirine are given; the country rock is ver rich in iron and has a high FeO : MgO ratio, while the sapphirine-bearing rocks a very low in iron and high in MgO, approximating to ternary mixtures of MgO, Al_2O and SiO_2.

OF the rock specimens collected by Mr. B. Stinear,[1] geologist for th Australian National Antarctic Research Expeditions during th 1954 operations, several from the Mawson area, MacRobertson Lan (fig. 1), were noted to contain irregular blue crystals mixed with a pa bronze mica. Microscopic examination of the blue material proved it be sapphirine; this mineral was subsequently found to be a regular co stituent of one particular group of rocks.

The rocks of the Mawson area are chiefly coarse-grained granitic typ carrying hypersthene. The sapphirine-bearing rocks are described b Mr. Stinear as forming an oval-shaped outcrop, some 20 feet by 15 fee of light coloured rock standing out in low relief from the surroundi dark brown country rock. Over the greater part of the outcrop the ro was of a uniform whitish colour, tinted pink or mauve. In what appear to be outer concentric zones, it graded into a whiter, more gneissic roc and then into a dark zone rich in biotite. As is common with rocks fro the Antarctic regions, the constituent minerals were fresh and unalter even on the surfaces that had been exposed to weathering.

Petrography.

The country rock. This is a dark brown quartz-felspathic rock contai ing many coarser crystals of brown felspar up to an inch in length. Und the microscope, felspars are seen to predominate over quartz, which

[1] Mr. Stinear is a geologist of the Commonwealth Bureau of Mineral Resour co-operating with A.N.A.R.E.

rather more finely granular than the felspars. Plagioclase forms larger crystals showing a variety of twin-laws—Carlsbad, Baveno, or pericline combined with albite twinning. The composition suggested by the maximum symmetrical extinction of albite twins is approximately $Ab_{45}An_{55}$—a labradorite. Orthoclase is present in approximately equal amounts, but as larger porphyritic crystals. Hypersthene, rather strongly pleochroic, comprises perhaps 5 % of the rock. From its colour and pleochroism, and the high FeO:MgO ratio in the rock analysis (table I, col. 1), it is evidently a ferriferous variety. With it are associated some apatite and magnetite.

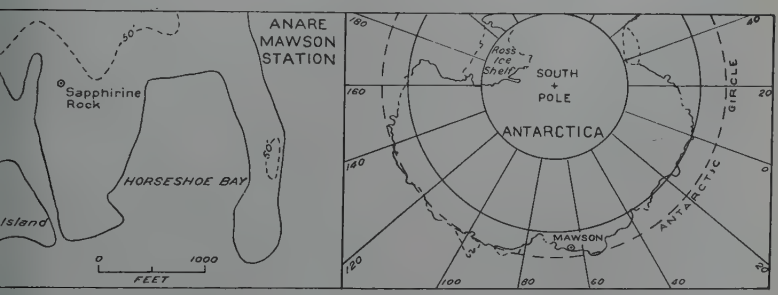

Fig. 1. Antarctica and the Mawson station.

The rock appears to be a characteristic member of the Antarctic charnockites.

Enstatite–sapphirine–spinel rock. This light blue-grey rock of medium grain size is typical of the material making up the greater part of the outcrop. In the hand specimen, especially on the weathered surface, bluish nodules up to 0·5 mm. diameter are clearly distinguishable from the white enstatite. Pale bronze flakes of mica are scattered irregularly through the rock.

Under the microscope the greater part of the rock is seen to be equigranular enstatite (average grain size approximately 0·3 to 0·4 mm. diam.). Of similar appearance, but less abundant and showing no cleavage, is some of the sapphirine; it occasionally forms a myrmekitic intergrowth with the enstatite. More commonly the sapphirine is concentrated in nodules with the spinel, which has almost the same refractive index. They are distinguished only by the weak birefringence of the sapphirine, which also shows a tendency to rim the spinel. The mica is a colourless phlogopite and shows a somewhat irregular distribution

through the sections. A chemical analysis of the rock is given in table I column 3.

Enstatite–sapphirine–cordierite rock. This occurs as a zone between th spinel-bearing phase of the outcrop and the dark outer band. It is white rock composed chiefly of enstatite and cordierite, bands rich i phlogopite, and scattered nodules of sapphirine. The cordierite is quit colourless and transparent, nearly always showing parallel multipl twinning. It contains no haloes, is coarsely crystalline, and frequentl contains small inclusions of enstatite. The enstatite is similar to tha in the spinel-bearing rocks, as is the comparatively small amount o sapphirine. A chemical analysis is given in table I, column 2.

The dark border phase. From the appearance of the specimens this probably rather a narrow band, perhaps only a few inches wide. It is dark gneissic rock, rich in dark mica, and frequently shows patches dark blue mineral on weathered surfaces. Some of the specimens als show a gradation into material resembling the country rock.

Microscopically, the predominant mineral is a light brown biotite. Mixe with this is a plagioclase of similar composition to that in the countr rock, and a pale hypersthene. The dark blue mineral of the hand specime is largely an iron-rich sapphirine associated with a little spinel; the are identical in appearance. In the specimens available there is son segregation of the ferromagnesian minerals. The biotite is more abu dant on the inside of many of the specimens, and the hypersthene mo abundant on the side that grades, rather sharply, into the country roc

Mineralogy.

Sapphirine occurs in most of the rocks in mauve-coloured aggregat with spinel, a few millimetres in diameter. In certain cases it occu pure as sky-blue grains 2 to 3 mm. across mixed with phlogopite on t surface of the specimen. This surface appears to have been part of vein or vug. The mineral was originally identified from such materi by its optical properties, which are: $\alpha = 1{\cdot}703$, $\gamma = 1{\cdot}710$, 2V near 8 positive. No cleavages were seen. The identity of the mineral was co firmed by X-ray powder photographs taken by Dr. B. J. Skinner. chemical analysis of the sky-blue material is included in table I.

Enstatite is white or pale grey in colour, and is common to all the lig coloured rocks. Its iron content is very low, probably of the order 2 % FeO. This is indicated partly by the low iron content of the roc as a whole, and also by its low refractive indices: $\alpha = 1{\cdot}655$, $\gamma = 1{\cdot}66$

Spinel is common in all the specimens from the centre of the outcro

It is very similar in appearance to the sapphirine, both in the hand specimen and in thin section. Its refractive index is 1·717, which suggests a practically pure magnesium spinel.

Cordierite is quite colourless, with refractive indices $\alpha = 1{\cdot}532$, $\gamma = 1{\cdot}540$, 2V close to 70°, positive. Commonly it is twinned on a

Table I. Chemical analyses of three rocks and of sapphirine from Mawson, Antarctica.

	1.	2.	3.	4.
SiO_2	63·12	46·34	38·00	16·71
Al_2O_3	14·29	23·21	23·58	54·77
Fe_2O_3	0·97	0·77	1·03	3·16
FeO	6·12	0·66	1·03	
MgO	2·07	24·00	32·57	19·89
CaO	4·32	0·36	0·16	1·13
Na_2O	2·96	1·24	1·72	0·20
K_2O	4·14	2·42	1·70	0·95
TiO_2	1·48	0·34	0·32	0·67
P_2O_5	0·41	—	0·02	—
SO_3	0·02	0·03	0·03	—
Cl	0·03	0·04	nil	—
MnO	trace	—	—	—
H_2O at 100° C. ...	0·17	0·08	0·07	0·21
H_2O over 100° C.	0·26	1·19	0·35	—
Ign.	—	—	—	1·90
Less O equiv. ...	0·01	0·01	—	—
Total	100·35	100·67	100·58	99·59

1. Charnockitic country rock, Mawson area.
2. Enstatite–sapphirine–cordierite rock.
3. Enstatite–sapphirine–spinel rock.
4. Sapphirine.

Analyses undertaken through the courtesy and co-operation of the South Australian Department of Mines. Analysts P. C. Hemingway and R. N. Lewis of the Geological Survey Laboratories.

parallel law. Occasionally it occurs in small veinlets one or two millimetres across, when it is quite colourless and transparent. The refractive indices of the mineral and the low iron content of the rock suggest that it is an almost pure magnesium cordierite.

Phlogopite is a pale bronze colour, uniaxial negative, with refractive indices $\beta = \gamma = 1{\cdot}570$; α was not measured.

Chemistry.

Chemical analyses of the country rock, the enstatite–sapphirine–spinel rock, the enstatite–sapphirine–cordierite rock, and sapphirine separated from a small vein are given in table I.

The most notable features of the analyses are the high iron conten and high FeO:MgO ratio in the country rock, and the very high mag nesia and low iron content of the sapphirine rocks. The latter, in fac approximate to ternary mixtures of the system $MgO–Al_2O_3–SiO_2$, thes three constituents making up some 95 % of the rocks.

The sapphirine analysis gives almost exactly the formula $Mg_2Al_4SiO_1$ or $2MgO.2Al_2O_3.SiO_2$. Other published analyses of sapphirine give, i most instances, compositions ranging from this to $Mg_4Al_{10}Si_2O_{23}$, c

TABLE II.

Madagascar (Lacroix and de Gramont, 1921) ...	$Mg_{2.00}Al_{4.16}Si_{1.00}O_{10}$
India (Muthuswami, 1949)	$Mg_{2.00}Al_{4.04}Si_{1.00}O_{10}$
Quebec (Warren, 1912)	$Mg_{2.00}Al_{4.00}Si_{1.00}O_{10}$
Mawson (this paper)	$Mg_{2.06}Al_{3.93}Si_{1.00}O_{10}$
Italy (Cornelius and Dittler, 1929)	$Mg_{3.83}Al_{10.00}Si_{2.08}O_{23}$
Transvaal (Mountain, 1939)	$Mg_{3.76}Al_{10.16}Si_{2.00}O_{23}$
Western Australia (Prider, 1945)	$Mg_{3.99}Al_{9.90}Si_{2.07}O_{23}$
Greenland (Ussing, 1889)	$Mg_{4.03}Al_{10.08}Si_{2.00}O_{23}$

$4MgO.5Al_2O_3.2SiO_2$. Table II gives the approximate formulae (reduce to Mg:Al:Si:O ratios) of sapphirine from eight localities, calculate from the various published analyses.

Foster (1950) found the best synthetic composition for sapphirine t be $Mg_4Al_{10}Si_2O_{23}$. Gössner and Mussgnug (1928) found the crystal stru ture to correspond to $Mg_2Al_4SiO_{10}$ in which MgSi is indefinitely replac by AlAl. This appears to be confirmed by the natural occurrences; mar of these correspond closely to $Mg_2Al_4SiO_{10}$, but by replacement (Mg,Fe)Si by AlAl grade into $Mg_4Al_{10}Si_2O_{23}$, which appears to be t limiting composition of the mineral, at least in nature.

Discussion.

The genesis of these rocks must remain in some doubt. They form small isolated outcrop in a large rather flat area of charnockites. N clear relation can be seen between the composition of the main part the outcrop and that of the charnockite, except for the magnesium co tents. It may be of significance that at least two other small isolate outcrops of magnesia-rich rocks occur in the Mawson area. One of the is largely composed of a diopside–spinel rock, and the other is a fo sterite marble. It is possible that these outcrops represent the remai of large xenoliths of magnesia-rich sedimentary rocks, which have be included in the charnockite and completely recrystallized.

The system $MgO–Al_2O_3–SiO_2$, both with and without water, h

been investigated intensively. In the original work on the dry system (Rankin and Merwin, 1918) sapphirine was not recorded. Foster (1950) predicted, and Kieth and Schairer (1952) confirmed the presence of a small field for this compound on the liquidus of the dry system. Yoder (1952) determined assemblages stable in the presence of an excess of water vapour at 15 000 lb. per sq. in. up to 990° C. and Roy and Roy (1955) covered the field at 10 000 lb. per sq. in. up to 780° C. In neither of these cases was sapphirine recorded. Yoder also gives a diagram for probable assemblages stable in water-deficient regions at approximately 600° C. and 15 000 lb. per sq. in. Again, sapphirine is not included in this diagram.

In the work on the hydrous system, less attention was paid to the alumina–spinel–silica part of the diagram, so that it is possible that sapphirine may still occur under those experimental conditions. It seems more likely, however, that sapphirine enters the assemblages under conditions of undersaturation with water.[1] This is in line with its natural occurrences. The two notable assemblages at Mawson are enstatite–sapphirine–spinel and enstatite–sapphirine–cordierite. These two assemblages are known from a number of localities, as is the corundum–sapphirine assemblage (fig. 2). Assemblages in the area cordierite–corundum–sapphirine are much more in doubt. Vogt (1947) discusses mineral assemblages with sapphirine, but leaves this area of his diagram open. He notes, however, that sapphirine and sillimanite have yet to be found together, even in areas where sillimanite occurs in associated rocks. Furthermore, cordierite–corundum is of such widespread occurrence under a variety of conditions that it may not be unreasonable to expect it to be a stable assemblage under the conditions for the formation of sapphirine. Therefore, it seems reasonable to accept the assemblages of fig. 2 for sapphirine-bearing facies of the type described here.

The approximate compositions, recalculated to mol. %, of the enstatite–sapphirine–spinel rock, the enstatite–sapphirine–cordierite rock, and the charnockite (substituting MgO for FeO) have also been plotted on fig. 2. They lie almost on a line, so that it seems reasonable to suppose that the cordierite-bearing phase is the result of reaction between the highly magnesian rock and the charnockitic country rock. The iron-rich investment of the outcrop is a well-known feature of the reaction between basic or acid xenoliths and host rock of the opposite nature. This, together with the occasional occurrence of other highly magnesian outcrops in the locality, suggests that these rocks may be isolated large xenoliths of siliceous magnesian sedimentary rocks, which

[1] See Appendix.

have been caught up in the original granitic magma and undergon complete recrystallization and partial reaction with the host, unde conditions of moderately high pressure and temperature and litt water.

Finally, it may be noted that further synthetic work on the syste

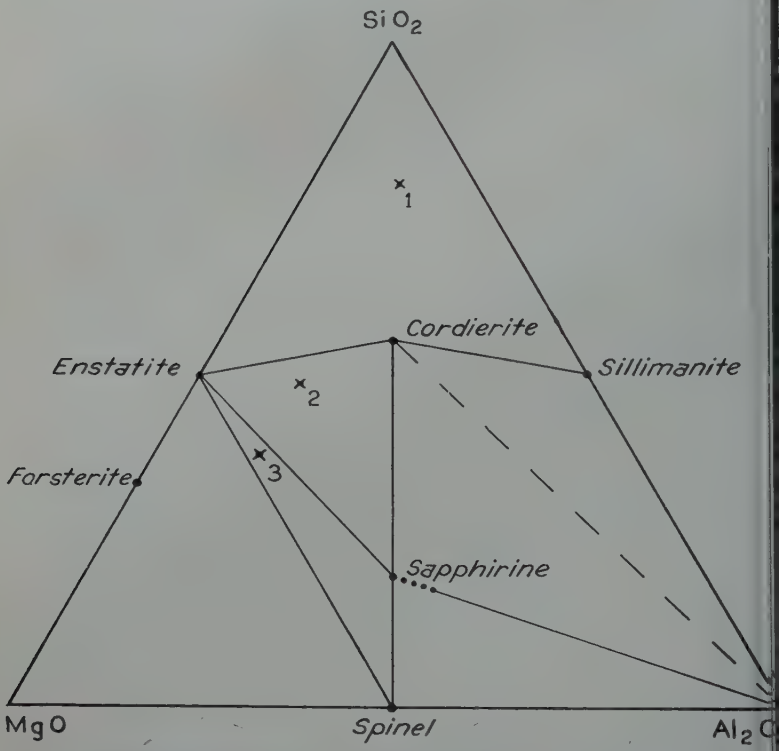

FIG. 2. Mineral assemblages in the system MgO–Al_2O_3–SiO_2. Crosses indicate approximate positions of rocks described in text. Mols. per cent.

MgO–Al_2O_3–SiO_2–H_2O under conditions of undersaturation with wate especially in the regions of the system where sapphirine assemblag might be expected to form, may give some precise information as t the temperature–pressure conditions under which these unusual rock were formed, and, as a corollary, as to the conditions under which th surrounding charnockites have formed.

Acknowledgements. The author wishes to record his thanks to Mr. B. Stinear f his co-operation in this work, and to Sir Douglas Mawson for much assistance gathering material for the preparation of the paper.

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APPENDIX (*see p. 695*)

Discussion with Dr. G. C. Kennedy of the Institute of Geophysics, University of California, Los Angeles, suggests that this is an erroneous premise. Water vapour pressures lower than total pressure may give rise to different assemblages. The mineral associations recorded in this paper may have been formed under such conditions, or may have been formed in a pressure range higher than has been yet investigated for this system.

SHORT COMMUNICATIONS

Kirschsteinite, a natural analogue to synthetic iron monticellite, from the Belgian Congo.

In a recent paper[1] the authors published brief descriptions of tw new silicates from a complex melilite–nephelinite lava from the crat of Mt. Shaheru, Nyiragongo area, North Kivu, in the Belgian Cong For these silicates the names götzenite and combeite, respectivel were proposed. The same nephelinite specimen, numbered S.80, co tains another major constituent which could not be identified micr scopically. In its optical properties and general appearance the miner shows some relationships to olivine. It deviates, however, from the mer bers of the forsterite–fayalite series and from monticellite. For th reason the mineral was subjected to a closer study. It proved to essentially an iron analogue of monticellite, $CaMgSiO_4$, and glauc chroite, $CaMnSiO_4$, and for this natural $CaFeSiO_4$ the name kirsc steinite is proposed, in honour of the German geologist, the late Dr. Eg Kirschstein, who died in the events of the World War I in East Afric As has been pointed out by Meyer,[2] Dr. Kirschstein was an early pione in the geological exploration of the Virunga volcanic field in North Kiv

The kirschsteinite-bearing specimen from the Shaheru crater contai the following minerals: clinopyroxene, melilite, nepheline, kalsilite, gö zenite, sodalite, kirschsteinite, combeite, magnetite, perovskite, apatit brown hornblende, and pale biotite. In addition, an unknown miner was found in sparing amounts, a study of which is in progress. Clos characteristics of these minerals and of the rock will be given elsewhe by Meyer and Sahama.[3]

The kirschsteinite was isolated from the rock with heavy liquids an a Frantz-type isodynamic separator. A microscopic test showed th material to be very pure. The result of the chemical analysis is: Si 32·71 %, TiO_2 0·23, Al_2O_3 0·26, Fe_2O_3 0·66, FeO 29·34, MnO 1·65, Mg 4·95, CaO 29·30, Na_2O 0·34, K_2O 0·36, P_2O_5 0·07, H_2O+ 0·25, H_2O- 0·0 total 100·18. The analysis corresponds to the following molecular co position: $CaFeSiO_4$ 69·4 mol. %, $CaMnSiO_4$ 4·3, $CaMgSiO_4$ 22·6, exce Fe_2SiO_4 3·7. Accordingly, the mineral is to be called magnesian kirsc steinite. The analysis shows a slight deficiency in calcium in relation the sum of iron, manganese, and magnesium. The most iron-rich mont cellite previously known from natural rocks is that from the Island

Muck, Scotland, with *ca.* 25 wt. % $CaFeSiO_4$.[4] A pycnometric specific gravity determination of the analysed material yielded $D = 3{\cdot}434$.

The indexed powder pattern, recorded with the Philips Norelco X-ray diffractometer, with filtered cobalt radiation and a silicon standard, is as follows:

hkl.	*I.*	$2\theta_{obs.}$	$d_{obs.}$	$Q_{obs.}$	$Q_{calc.}$
020	35	18·485	5·569	0·0322	0·0323
021	25	24·56	4·205	0·0565	0·0565
001	10	26·67	3·878	0·0665	0·0666
111	70	28·305	3·658	0·0747	0·0747
002	10	32·35	3·211	0·0970	0·0970
130	100	35·31	2·9492	0·11497	0·11498
040	25	37·495	2·7830	0·12911	0·12912
131	85	38·995	2·6798	0·13924	0·13924
112	80	40·18	2·6040	0·14747	0·14746
041	15	40·985	2·5549	0·15319	0·15338
{140 / 122	40	43·49	2·4143	0·17156	{0·17147 / 0·17167
210	15	44·26	2·3744	0·17737	0·17747
211	10	47·405	2·2251	0·20197	0·20173
132	10	48·635	2·1721	0·21195	0·21202
240	60	58·505	1·8304	0·29847	0·29852
{160 / 133	10	62·16	1·7326	0·33312	{0·33287 / 0·33332
152	10	62·945	1·7132	0·34070	0·34114
062	30	67·65	1·6068	0·38732	0·38756

The indexing was based on the data for fayalite that has been given by Yoder and Sahama.[5] Unit-cell dimensions, calculated from the powder pattern, are as follows (±0·005 Å.): a 4·859, b 11·132, c 6·420 Å. The crystallographic axes were selected in a way that corresponds to that generally accepted for the forsterite–fayalite series. A series of rotation and Weissenberg photographs about the three crystallographic axes confirms the unit-cell dimensions given. Systematic extinctions are similar to those for forsterite.

When viewed in specimen under the binocular microscope, the mineral shows a very slight greenish colour. In thin section it is colourless. The optical properties are: α 1·689, β 1·720, γ 1·728, $\gamma-\alpha$ 0·039 (calc.), $2V_a$ 1°±1° (universal stage), $2V_a$ 53° (calc.). The optical orientation was tested with a thick Berek compensator on crystals mounted on the goniometer head of the Weissenberg camera. Comparison of optical tests and rotation photographs results in the following relationship between the axes of the unit cell and of the optical indicatrix: $a = \gamma$, $b = \alpha$, $c = \beta$. This optical orientation corresponds to that of the forsterite–fayalite series.

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Th. G. Sahama
Kai Hytönen

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The nature of batchelorite.

THE name batchelorite was given by W. F. Petterd[1] to a green sla mineral found in the Mt. Lyell Mine, Tasmania. He gave the compos tion as $H_2O . Al_2O_3 . 2SiO_2$, a hydrated silicate of aluminium, but adde in parenthesis, that the analysis[2] was made on green nodules in the schis It is evident, therefore, that the composition of batchelorite itself w never determined.

A specimen of batchelorite in the British Museum (B.M. 1956, 30 which, although not a type specimen, was collected from the ty locality and conforms in appearance with the type mineral, has be shown by its optical properties and X-ray powder pattern to be musc vite schist. A chemical analysis confirmed this and revealed also th the mineral contains a small proportion of chromium. The analys given below, corresponds to the formula:

$$(Na,K,Ca,Ba)_{1.00}\,(Al,Ti,Fe,Cr,Mg)_{2.03}\,(Si,Al)_4\,O_{10.04}\,(OH,F)_{1.98}.$$

There would now appear to be no justification for the retention of t mineral name batchelorite.

Batchelorite from Mt. Lyell, Tasmania (B.M. 1956, 300).

SiO_2 ...	45·1 %	CaO ...	0·7 %	$H_2O(-)$ ...	0·3
Al_2O_3 ...	36·4	MgO ...	1·2	$H_2O(+)$ ...	4·0
TiO_2 ...	0·4	Na_2O ...	1·5	F ...	1·0
Fe_2O_3 ...	0·5	K_2O ...	8·8	MnO ...	nil
Cr_2O_3 ...	0·3	BaO ...	0·3	Total ...	100·5
				less O for F ...	0·4
					100·1

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[1] Catalogue of the Minerals of Tasmania, 1910, p. 22, no. 39.
[2] SiO_2 49·4, Al_2O_3 45·1, H_2O 5·6, total 100·1 %.

Beaverite from the Lake District.

BEAVERITE ($Pb(Cu,Fe,Al)_3(SO_4)_2(OH)_6$) was first recognized and iden fied by us as a British mineral in 1949, the occurrence being brie recorded in 1952.[1] The first suspected specimens were examined spect graphically and they (as well as others found subsequently) were c

irmed by powder-photographs showing exact agreement with those of sample of the type-material from Beaver Co., Utah, U.S.A., supplied by Dr. W. T. Schaller, who first described it.

In all the foreign occurrences so far recorded, beaverite is described as forming powdery aggregates of microscopic hexagonal plates: this is its usual habit in Cornwall and Cumberland, but at one locality in the latter county we have found it in small but well-defined rhombohedra. Examination of a large number of specimens collected in the Lake District has shown that many are derived from alteration of beudantite ($PbFe_3(AsO_4)(SO_4)(OH)_6$), another isomorphous member of the group, and that others are intermediate minerals in various stages of alteration. In addition to some of these intermediate members, well-defined beaverite has been found at the following localities in the Lake District:

Higher Brandy Gill, Carrock Fell; first found here in 1949 and subsequently in considerable amounts in the outcrop of an east–west Cu–Pb–As vein on the west side of the gill a short way below its head, as bright canary-yellow powdery aggregates derived from direct alteration of galena and still showing its cubic cleavages (B.M. 1956, 83), also as small, yellow to greenish-yellow powdery masses in cavities in vein quartz originally occupied by sulphides, and as yellow, greenish-yellow, and brownish-yellow drusy, crystalline crusts, derived from alteration of beudantite (itself mainly derived from alteration of carminite, $PbFe_2(AsO_4)_2(OH)_2$), coating cavities and joints both in the vein-material and the wall-rock. The sequence carminite → beudantite → beaverite can be well seen on many specimens.

Driggith Mine, Caldbeck; yellow to golden-yellow and golden-brown powdery aggregates on cerussite and altered galena in the outcrop of the vein, associated with other minerals beudantite → beaverite and beudantite → plumbojarosite.

Netherrow Brow, Caldbeck; yellow to greenish-yellow, powdery beaverite, with beudantite and other secondary arsenates in oxidized vein-material from a north-west–south-east vein, carrying Pb–Zn–Fe–As–Cu sulphides, tried from an old cross-cut near its outcrop between Sandbed and Potts Gill mines.

Netherrow Brow, Caldbeck; yellow powdery aggregates, with earthy brown beudantite and plumbojarosite, in similar vein-material from an old level, half a mile to the north-west of and probably driven on the same vein as the preceding, near the farm of Nether Row.

Potts Gill Mine, Caldbeck; in oxidized vein-material from a small Cu–Pb–Zn–As vein cut by the old no. 1 cross-cut (of the barytes mine)

near the head of the Gill Beck, beaverite has been found as light canar yellow powdery aggregates with small brilliant crystals of brochant (B.M. 1956, 82), and as small (0·5 mm.) brilliant, well-formed yell rhombohedra in the same matrix. This appears to be the first report occurrence of beaverite in this habit.

Ingray Gill, Caldbeck (between the hamlet of Fellside and Hay Gill); light yellow powdery coatings on decomposing galena in vein-mater from the northernmost of the two old cross-cuts near the head of the g The vein is obscured by drift but appears to run roughly NNW. an from material on the dumps, apparently contains Cu, Pb, Zn, Fe, As, a traces of Co, Ni, Mo, V.

Higher Roughtongill, Caldbeck; as yellow, powdery masses, with ja site and chrysocolla, in somewhat chalcedonic quartz from the outcr of the main Roughtongill South Vein along the flank of Balliway Rig

At several of these localities, intermediate beudantite–beaver minerals also occur.

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[1] A. W. G. Kingsbury, Trans. Roy. Geol. Soc. Cornwall, 1952, vol. 18, pt. p. 394.